1. General responses to Referee reviews

We thank the referees for their thorough review and their useful suggestions for improving both, the presentation of our work, and the interpretation of our data.

We also thank the Editor for extending twice the deadline for submitting our responses.

In order to fulfill the major referees' requirements, the revised manuscript has been deeply changed and re-written; in particular:

- A better focus on our (new) scientific objectives is now presented in the revised introduction;
- The sequencing and the link between the different sections has been improved;
- A better description of how we used the MEGAN model is now given in a new specific section (section 2.5); in particular, we explain how we did run MEGAN2.1 using our in situ data (wilting point, seasonal emission factors, …);
- We present the sensitivity of MEGAN2.1 performance over a large range of wilting point values;
- We now give some suggestions on how MEGAN model could be improved in order to better account for drought stress of drought adapter isoprene emitters;
- As we agreed that our dataset was neither large nor robust enough for capturing future emission under RCP scenarios, the '2100 projections' are no more considered; instead, we present the sensitivity of *Q. pub.* isoprene emissions to expected future climate changes for 6 different cases: moderate and severe T changes, moderate and severe P changes, moderate and severe T+P changes;
- Further information has been added, in particular, in the 'Materials and Methods' concerning which version of MEGAN was used, the ANN limitation and uncertainty, how the exclusion system was operated during our experiment, how ORCHIDEE model was used and what for, and how the COOPERATE dataset was used;
- A conclusion has been added

Consequently:

- The sections 3.3 and 3.4 ('Results') and 4.2 and 4.3 ('Discussion') were completed re-written;
- A new title is now proposed to better fit with the scope of the revised manuscript ("Seasonal variations of *Q. pubescens* isoprene emissions from an *in natura* forest under drought stress and sensitivity to future climate change in the Mediterranean area");
- The order and title of some sections of the 'Materials and Methods' has been changed, and a new section 2.5 is now dedicated to the version of MEGAN we used;
- Except for Fig. 1 & 2, all other figures are new, and 2 tables have been added;

Eventually, in order to make the reading smoother and the understanding clearer the manuscript has been proofread (see certificate).

2. Responses to Referee #1

2a. General comments

None

2b. Detailed comments

We do thank Referee #1 for his/her careful review and comments.

Abstract

Line 1: ‘physiology’ has been changed by ‘gas exchange’ (and all along the document as well).

Lin 20-23: the lowest ER values in October and April, 6 and <2 µg gDW^{-1} h^{-1} respectively, have been added.

Lin 20: no, the lowest Gw values were observed between July and September (<20 $mole_{H2O}$ m^{-2} s^{-1}) not in April (figure 2b).

Line 22: we do not understand this point; emission rates ER (measured values) are different from emission factors Is (=ER normalized to temperature and PAR).

Materials and Methods

Pg 5 Lin 10: sampling volumes varied between 0.45 and 0.9 L depending on the season and the hour of the day, thus, on the expected emission intensity. This precision is now given in the revised section 2.2.

Pg 8 Lin 7: a new web site link is now given in the revised section 2.7.

Results

Pg 9 lin 31: no, PAR peaks in June 13 (899.3 µmole m-2 s-1).

Pg 10 Lin 20: further information is now available in the revised sections 3.2 and 4.1 (Electric resistivity tomography measurements have shown the heterogeneity of the karstic substrate organized as soil pockets developed between limestone rocks. Water and nutrient pools and dynamics probably differ greatly between the shallow upper soil layers and the soil pockets developed between limestone rocks. However, the soil trenches carried out in the site have shown that a calcareous slab often developed at a depth of 10-20 cm and that the roots of the oaks were rather distributed in this superficial humiferous horizon, and that only a few large roots cross this slab.)

Pg 10, Lin 26: Senescence of leaves: although senescence had just begun during this sampling period, but we did check that the enclosed branches were not senescent during our measurements. This information is now given in the revised section 2.2.

Discussion

Point 1: As already mentioned, the water availability from deep roots is now better discussed in the revised discussion, section 4.1.

Point 2: we do consider moderate to more severe drought effects; this is why we mentioned the overall range of drought intensity.

Point 3: we suggest that the frequency over which the different environmental parameters (not only light) should be larger than the one considered so far, and how these frequencies are changing over the year (see new section 4.2 and conclusion).

Pg 13, lin 15: although this section has been completely re-written we made sure to put Q. Pub in italics in the document.

Pg 15, lin 12: this section has been completely re-written.

Pg 16, lin 9-16: this section has been completely re-written.

Figure caption

Same colors of the legends in all graphs: we used blue and red colors for ND and AD respectively in all graphs; therefore, we are not quite sure to understand what referee#1 wants.

Pg 23, lin 3: July 2013 was changed to June 2013.

Pg 23, lin 9 & 18: 'June 2013' was added.

Pg 23, lin 18: Since Fig. 3 has been changed a new figure caption is now given.

Fig 1: in Fig. 1 (and other figures as well) the colors do differ from ND (blue) and AD (red) treatment. However, PAR and T values being the same for both plots, this color code was deliberately not used for PAR and T.
Legend axis was reissued as suggested and a vertical line between 2012 and 2013 was added.

Fig 2: we did not add 'isoprene' as suggested to keep the title short; ER and Is meanings are given in the figure caption and, anyway, all the paper is about isoprene (and not another VOC) emissions.

Fig 3: Former figure 3 was changed by a new one.
Fig 4: Former figure 4 was removed.

Fig 5: Former figure 5 was removed.

3. Responses to Referee #2

We do thank Referee #2 for her/his careful reading and useful comments and suggestions.

3a. General comments

- Use of literature values instead of site-observed data: G14 was tuned using O3HP data, not literature data; this point is now more clearly explained in the new section 2.5.
- No discussion of potential uncertainties from G14 and ANN in general: details are now given in the revised section 2.6 and discussed in the new section 4.3. (Among the other available statistical methods, ANNs present the advantage of being the most parsimonious (e.g. giving the smallest error for a same number of descriptors; see for instance Dreyfus et al., 2002). Moreover, ANN approach, as the other non-linear regression methods, is not, or not very, sensitive to regressors' co-linearity (Bishop, 1995; Dreyfus et al., 2002). One of the ANNs limitations is that they can be used only for interpolation, not extrapolation exercises. For this reason, our future RCP projections we made using only xi values that did fit into the range of variation of xi obtained during the training phase; in total 21% of data were thus rejected. ANN optimization during the training phase was based on the reduction of the root mean square error (RMSE) between calculated and measured values. Our final optimized RMSE (validation data) was 8.5 µg gDW^{-1} h^{-1} for our ER values ranging between 0.06 and 113 µg gDW^{-1} h^{-1}, and represents 35% of the mean (22.7 µg gDW^{-1} h^{-1})).
- No comparison with process based model: as mentioned in the first paragraph, p3 of the original document, process based model require a complex set of data to be ran; such a dataset is not available for this study. This is the reason why an 'empirical' model (MEGAN) was solely tested.
- No conclusion and no clear key messages: a new conclusion has been added, and key messages are now given.
- Abstract:

Too many abbreviations: we cannot use less than the 4 remaining abbreviations (ER, ND, AD, G14) if we want to keep the abstract as concise as possible.

Sentences were added at the beginning of the abstract in order to better explain 'why we need this study'.

- Method:

No description of MEGAN: a complete description of the MEGAN2.1 model and how it was tuned in our study is now given in a new specific section 2.5.

Better description on how ORCHIDEE data were used and how G14 was tuned: the purpose of running ORCHIDEE and how the ISI-MIP and ORHCIDEE derived data were used in our G14 algorithm is now detailed in sections 2.6, 2.7, 2.8 and 3.4.

A more detailed description on how AD roof was operated is now given in section 2.1.

- Results:

Use of on-site data to apply MEGAN rather than 'literature' data: detailed information is now given in the new section 2.5.

- Discussion:

Long text on future ER although no consideration on C source + training period for G14 is too short: C source was indeed not directly considered since the hypothesis we made in applying a neuronal approach to statistically analyze our data was to consider ‘simple’ integrative environmental parameters; C source, nor vegetation adaptation, were thus not considered, but *in fine* we hypothesized that they are, more or less indirectly, driven by PAR, T, SW and ST fluctuations over a range of different frequencies.

As vegetation adaptation is concerned, we did discuss this point at the end of the original section 4.3 (p 17) since we are aware that this aspect is of importance. This point is also mentioned in our revised and new section 4.3.

Thank you: we do agree that our database was not large enough to really assess impacts under future climates such as RCP2.6 and RCP8.5. In the revised manuscript, the future climatic data are now used only to test the sensibility of isoprene emissions to T, P and T+P changes.

No conclusion: As mentioned earlier a proper conclusion is now given at the end of the manuscript.

3b. Detailed comments

- ‘gaz’ has been changed to ‘gas’.
- P3, L5, References for empirical-based model: Ashworth et al. (2013) is actually a review where both types of models (empirical and process based) are described.
- P3, L31 and P3, L32: this part of the introduction has been changed, but we made sure that to explain an abbreviation when used for the first time.
- P4, L3-8: thank you; the scientific questions considered in our work are now better explained at the end of the introduction, and in the “results” and “discussion”.
- P4, L26: this sentence has been rewritten at the beginning of the revised section 2.2.
- P4, L27: ‘except from’ has been changed as requested in the revised section 2.2.
- P5, L22: only a small fraction (<5%) of the data was missing ; of course, the bias between Pcum curves at both sites was assessed and considered to ‘extrapolated’ the missing values at the O3HP site. As the precipitations were cumulated over 7, 14, 21 days, the bias was negligible (around 1%) and no adjustment was made. This information has been added in the revised section 2.7.
- P6, L18: AF is dry leaf mass per area conversion factor, called LMA in the previous line. AF was hence changed by LMA in the revised section 2.3 (former section 2.4).

All the abbreviations cited were homogenized, in the text and in the figures.

- P6, L23: Cout and Cin order has been changed in the revised section 2.3.
- P8, L1: How Krustal-Wallis test detects seasonal variation? Kruskal-Wallis tests allowed to check for different median values among months. ANOVA tests could not be used since data did not follow the requirements of parametrical tests. This information has been added in the revised section 2.4 (former section 2.5).
- P9, L31: we clarified in the revised section 2.1 how the rain exclusion of 30% was achieved along the seasons.
- P10, L2-5: although, in the absolute, the gap between Pcum(AD) and Pcum(ND) curves increases toward the end of 2012, from July 2012 the relative difference between both curves was maintained at a ≈ 30 % (fig. 1c: 510 and 760 mm respectively, thus a 33 % reduction) .

- P10, L11/P5 L17-19: we clarified in the revised section 3.1, why, although PAR measured in the COOPERATE database was made on one point above the canopy, the PAR actually received by the enclosed branch in the chamber could be different from one branch to another, especially in September 2012,during the autumnal sun setting.
- P10, L22-23: this line has been removed
- P11, L2: 'P=3.9' was a mistake and was removed.
- P11, L5-9: because the measurements were made right during the beginning of the isoprene onset period, some of the sampled branches started to emit isoprene significantly, while others emitted only at a very low level; this led to a large variability that could not be significantly related to the relative position of the branches in the AN or ND plots. Further precision is now given in the revised section 3.2.
- P11, L13-14: these points have been already mentioned in our general responses and are now detailed in the new section2.5 dedicated to MEGAN 2.1 description.
- P11, L18: specific regression lines/R^2 are now given when needed in the document and/or in the Fig or Tables.
- P12, L6-7: thank you, our text was indeed not precise enough; we meant that under AD 'the contribution of the two lowest frequencies (-14 and -21 d.), was, RELATIVELY to the contribution of the two highest frequencies (instantaneous and -7d.), higher in April (48%) and June (700 and 40 % in 2012 and 2013 respectively) than during the summer (22, 8.5 and 16 % in July, Aug. and Sept. respectively)'. The text has been changed accordingly in the revised section 3.3.
- P12, L9: the contribution to each frequency has been converted to ratio and is now presented in the revised fig. 6 (former Fig. 4).

Note that the discussion concerning the relative contribution of each environmental parameter is no longer made: indeed, SW appeared as the 'major' driving regressors tested in G14 … since this was the ONLY regressor that differed between both sample sets (ND and AD).

- P12, L30: this section has been completely re-written, but we made sure to use correct number of RCPs in the revised text.
- P12, L31; P13, L17: these parts of the text have been completely re-written.
- P14, L5: thank you, 'µgC gDM-1 h-1' is now the only unit used for emission rates throughout in the revised text.
- P14 L28-31 and P15, L21-24: as explained earlier, and in our General Responses, the 'MEGAN adjustment' to our local data is now explained in the new section 2.5.
- P16 L2-3: 'degree day' unit was changed to 'Dd' and explained when it appeared for the first time in the revised section 4.2.
- P16, L12: soil water description by land models is no more addressed in the revised manuscript.
- Section 4.3: as mentioned in our General Responses, this section has been completely re-written. As suggested, sensitivity tests are now presented.

Concerning the comparison with other literature data, in the new conclusion we are now insisting on the fact that there is actually no in situ isoprene data comparable to our O3HP database; however, in the new section 4.3 we are now giving more details on the findings obtained during a seasonal study carried out on isoprene emission from *Q. pub.* saplings by Genard-Zielinski et al. (2015). In order to extend our discussion on species emitting other BVOC than isoprene and compare our results to other in situ drought study in the Mediterranean area, we are now reporting in the revised section 4.1 the Lavoir et al. (2009) study.

- Figure1: an x axis legend has been added also on the top of the (a) graph in order to make the reading easier.
- Figure 2: letter 'c' and 'd' meaning is now added in the revised figure caption of figure2.

Indeed, differences between ND and AD using Mann-Whitney tests should be denoted with asterisks at the top of each figure. Differences among months were tested using Kruskal Wallis tests (W) followed by followed by Newman-Kruels post-hoc test with a<b<c<d. These corrections have been made in the revised Figure caption.

Note that the Gw unit should be 'mmol cm^{-2} s^{-1}' as indicated in the revised document and not 'mol cm^{-2} s^{-1}' as previously written.

- Figure 3: former Fig. 3 was removed and replaced by a new one.

However, on this figure and others, log scale was not always suitable since, as explained in the discussion, many ER were set to zero by MEGAN2.1.

- Figure 5: Former Fig. 5 was removed and replaced by a new one.

4. Responses to Referee #3

We do thank Referee #3 for her/his thorough reading and useful suggestions. We tried, in particular:

- to better explain how we tuned MEGAN2.1 model in order to assess its ability in reproducing the effect of drought on Q. Pub ER ;
- to study the sensitivity of MEGAN2.1 to the wilting point value;
- to suggest some improvement in the formulation of the drought activity factor used in MEGAN2.1.

4a. Main concerns:

- Bibliographical weakness:

  Although many of the references cited in our manuscript were not all narrow in focus and scope, and that a large number of them did focus on the effects of drought onto photosynthesis/cellular processes/isoprene emissions (Chaves et al., 2002; Lichtenthaler et al., 1997; Funk et al., 2004, Simon et al., 2005; Tani et al., 2011; Guenther et al., 2013; Wiberley et al., 2005; Llusià et al., 2008, 2009; Owen et al., 1998; Loreto and Schnitzler, 2010; Pegoraro et al., 2004), we have added the works of Sharkey and Loreto (1993), and Brili et al. (2007).

  In the original paper, we did refer twice to the Peñuelas and Staudt (2010) paper (in the Introduction p2 and in the Discussion p16 of the former version), which is a review, and inherently, cannot be considered as narrow in scope.

  Our manuscript does not aim at reviewing all the isoprene modelling studies based on MEGAN; however the excellent work of Müller et al. (2008) is now cited in the revised manuscript, and their assessments of the sensitivity of isoprene emissions to soil moisture is now mentioned in the revised section 3.3.

  As now clearly explained (in the revised introduction and discussion), the assessment of the wilting point θw in the Sindelarova et al. (2014) study was based on the Pegoraro et al. (2004) work.

- Measurements:

  1. We have now made it clear in the revised manuscript (new section 2.5) that:

  - we did not aim at extrapolating – using MEGAN or any another emission model – isoprene fluxes from the whole canopy; our focus was to test MEGAN in assessing the impact of ND and AD on isoprene emission rates as observed from the sunlit branches of Q. pub; the effect of the canopy structure is thus not addressed in this paper (even if some measurements were made under the canopy during this study, see next paragraph).

  - the shading effect was investigated, only for 2 trees in the ND plot, and only in June 2012; we observed that, although the shading effect can be strong (PAR lowered by a factor of 6 to 18), measured isoprene emission factors (Is) were not significantly different (P>0.05) at the top and below the canopy (77±3 and 59±12 µg gDM^{-1} h^{-1} respectively); these points have been detailed in another paper (Genard-Zielinski et al., 2015).

  2. We give in the revised section 2.2 a full description on how the roof was operated in order to simulate an AD.

  When this study was conducted we were well aware that the future climatic changes will affect not only the intensity of the precipitations but its seasonality too (see our discussion on that point). Since our study started just after the roof operation was available, we did focus, for this 1st year of measurements, only on the exclusion intensity aspect rather than its 'timing'.

3. We don't see any scientific basis for which Referee#3 could state that we do relate the reality of our field work. Yes, a tremendous effort was made at the O3HP to conduct our field work and yes, we did sample Q. pub. over one week per month, as detailed in the table below.

Month	**Sampling dates**
June 2012	1 - 16
July 2012	15 - 20
August 2012	19 - 24
September 2012	18 - 24
October 2012	22 - 26
April 2013	22 - 27
June 2013	16 - 22

Note that we did not state that we sampled isoprene 'one week per month from June 2012 till June 2013'; we did precise that 'measurements were performed at least during one week, once a month, from June 2012 to June 2013, except from November 2012 to March 2013 when Q. pubescent is fully senescent with leaves remaining on the tree' (P7, L26-28).

All isoprene measurements presented here were sampled on cartridges except during April 2013 where only on-line PTRMS was used (and no cartridges). An intercomparison between Cartridge+GCMS and PTRMS was carried on parallel on another emitter present on the site (Acer monspessulanum); no significant difference was observed between both techniques. This information is now given in the revised section 2.3.

4. The COOPERATE data:

As now mentioned in the revised section 3.3, ANN training and validation were carried out using data measured at the O3HP (sampled ER, COOPERATE environmental data); we now explain in the revised manuscript that daily averaged values were used when regressors were cumulated over 7-21 days.

As mentioned in our response to referee#2, only a very few number (< 5 %) of precipitation data needed for assessing P integrated over 7, 14 or 21 days, was missing. As we spent quite a lot of time on the field site, we are well aware that precipitations can, locally, be highly variable in time and space; this is why we used the relative differences observed between the 2012 and 2013 Pcum curves in both sites (Forcalquier and O3HP) in order to 'fill the gap' of the missing data. Due to the fact that the P was integrated over 7, 14, 21 days, this bias remains negligible. These detailed are now given in the revised section 2.7.

Statistics

1. Being aware that MEGAN does include some 'historical' dependence of environmental conditions (as mentioned P15, L19-20 of the original manuscript) we did consider the PAR and T over the previous 24 and 240 hours before our measurements when we calculated isoprene emissions. This information is now clarified in the new section 2.5.

The other different points raised by Referee#3 concerning how we used MEGAN (canopy structure, canopy loss) are also detailed in the new section 2.5.

2. As mentioned earlier, no more 2100 projections are presented in the revised manuscript.

3. Indeed ANNs are often referred to as a ‘grey’ box, since such a statistical approach does not aim at providing new mechanistic understandings of the studied process. On the other hand, when a mechanistic approach is failing to do so, ANNs can provide some fruitful information. Note in particular that in MEGAN the isoprene dependency to PPFD over the previous 24 and 240h was deduced by a ‘best statistical fit’ (P3190, L28-32 Guenther et al., 2006), without providing any precise mechanistic insight on how and why it is working; the useful of MEGAN is, nevertheless, not challenged.

In our case, by using G14 we showed that, for a drought adapted emitter, isoprene emission shall be much more sensitive to T than to P under future climatic changes; MEGAN2.1 was unable to do so, since not ‘adapted’ to account for drought effect of a drought adapted isoprene emitter.

ORCHIDEE
A better description of what data were obtained by ORCHIDEE and how these data were used in G14 is now given in the revised sections 2.7, and 3.4.
Our projections were not made specifically for the O3HP site, but for a Mediterranean site representative of the O3HP site conditions. Therefore, precipitations –or other parameters – were not downscaled to the O3HP site.

4b. Recommendations

We followed the final recommendations made by the referee#3:

- As it is now explained in the new section 2.5, site-specific data were used for MEGAN2.1 assessment.
- Site data were also used for G14 development (as explained in the revised section 3.3)
- Site data (COOPERATE) were also used in G14 to assess the present case in the sensitivity tests (see revised section 3.4)
- The sensitivity of MEGAN2.1 to the wilting point is now presented in the revised sections 3.3 and 4.2.

However, as explained in the original manuscript, and as it is now mentioned twice in the revised manuscript, physiological parameters such as sap flow, transpiration, … were not measured during this work since it was not the aim of this work. Rather than using such complex data, we favored the use of more ‘integrative’ environmental variable, ‘easily’ accessible than complex physiological data; we hypothesized that, *in fine*, sap flow, transpiration, … are more or less indirectly driven by L, T, SW, ST, especially if they are considered over a large of frequency range as in G14.

5. New references cited in our responses

Brili, F., Barta, C., Fortunati, A., Lerdau, M., Loreto, F., and Centritto M.: Response of isoprene emission and carbon metabolism to drought in white poplar (*Populus alba*) saplings, New Phytol., 175(2), 244-254, 2007.

Lavoir, A.V., Staudt, M., Schnitzler, J.P., Landais, D., Massol, F., Rocheteau, A., Rodriguez, R., Zimmer, I., and Rambal, S.: Drought reduced monoterpene emissions from the evergreen Mediterranean oak *Quercus ilex* : results from a throughfall displacement experiment, Biogeosciences, 6, 1167-1180, 2009.

Sharkey, T. D., and Loreto, F.: Water-stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves, Oecologia, 95, 328–333, 1993.

Proof-Reading-Service.com
PhD theses, journal papers, books and other professional documents

Proof-Reading-Service.com Ltd, Devonshire Business Centre, Works Road, Letchworth Garden City, Hertfordshire, SG6 1GJ, United Kingdom
Office phone: +44(0)20 31 500 431
E-mail: enquiries@proof-reading-service.com
Internet: http://www.proof-reading-service.com
VAT registration number: 911 4788 21
Company registration number: 8391405

29 March 2018

To whom it may concern,

RE: Proof-Reading-Service.com Editorial Certification

This is to confirm that the document described below has been submitted to Proof-Reading-Service.com for editing and proofreading.

We certify that the editor has corrected the document, ensured consistency of the spelling, grammar and punctuation, and checked the format of the sub-headings, bibliographical references, tables, figures etc. The editor has further checked that the document is formatted according to the style guide supplied by the author. If no style guide was supplied, the editor has corrected the references in accordance with the style that appeared to be prevalent in the document and imposed internal consistency, at least, on the format.

It is up to the author to accept, reject or respond to any changes, corrections, suggestions and recommendations made by the editor. This often involves the need to add or complete bibliographical references and respond to any comments made by the editor, in particular regarding clarification of the text or the need for further information or explanation.

We are one of the largest proofreading and editing services worldwide for research documents, covering all academic areas including Engineering, Medicine, Physical and Biological Sciences, Social Sciences, Economics, Law, Management and the Humanities. All our editors are native English speakers and educated at least to Master’s degree level (many hold a PhD) with extensive university and scientific editorial experience.

Document title: **Simulating precipitation decline under a Mediterranean deciduous Oak forest: effects on isoprene seasonal emissions and predictions under climatic scenarios**

Author(s): **Anne-Cyrielle Genard-Zielinski et al.**

Format: **British English**

Style guide: **Biogeosciences at https://www.biogeosciences.net/index.html**

Seasonal variations of *Q.* ~~Simulating precipitation decline under a Mediterranean deciduous Oak forest: effects on~~*pubescens* isoprene ~~seasonal~~ emissions from an *in natura* forest under drought stress and ~~predictions under climatic scenarios~~sensitivity to future climate change in the Mediterranean area.

Anne-Cyrielle Genard-Zielinski[1,2], Christophe Boissard[2], Elena Ormeño[1], Juliette Lathière[2], Ilja M. Reiter[3], Henri Wortham[4], Jean-Philippe Orts[1], Brice ~~Temine~~Temime-Roussel[4], Bertrand Guenet[2], Svenja Bartsch[2], Thierry Gauquelin[1] and Catherine Fernandez[1]

[1]Institut Méditerranéen de Biodiversité et d'Ecologie marine et continental, Aix Marseille Université-CNRS-IRD-Univ. Avignon, Marseille, 13331CEDEX 3, France

[2]Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Gif-sur-Yvette, 91191, France

[3]Fédération de Recherche 'Ecosystèmes Continentaux et Risques Environnementaux', CNRS FR 3098 ECCOREV, Technopôle de l'environnement Arbois-Méditerranée, Aix-en-Provence, 13545, France

~~[4] Laboratoire~~[4]Laboratoire de Chimie de l'Environnement, Aix Marseille Université, CNRS, UMR 7376, Marseille, 13331, France

Correspondence to : Christophe Boissard, ~~(~~christophe.boissard@lsce.ipsl.fr~~).~~

~~**Abstract.**~~ **Abstract.** At a local level, biogenic isoprene emissions can greatly affect the air quality of urban areas surrounded by large vegetation sources, such as in the Mediterranean region. The impacts of future warmer and drier conditions on isoprene emissions from Mediterranean emitters are still under debate. Seasonal variations of *Q. pubescens* gas exchange~~Seasonal variations of Q. *pubescens* physiology~~ and isoprene emission rates (ER) were studied from June 2012 to June 2013 at the O_3HP site (French Mediterranean) under natural (ND) and amplified (+30%, AD) drought. While AD significantly reduced ~~the~~ stomatal conductance to water vapour ~~over~~throughout the ~~season~~research period excepting August, it did not significantly ~~limit~~preclude CO_2 net assimilation, which was ~~the~~ lowest in summer~~.~~ (≈ -1 µmol$_{CO2}$ m^{-2} s^{-1}). ER followed a significant seasonal pattern~~, whatever the~~ regardless of drought intensity, with mean ER maxima of 78.5 and 104.8 µgC g$_{DM}$$^{-1}$ h^{-1} in July (ND) and August (AD) respectively~~.~~, and minima of 6 and <2 µgC g$_{DM}$$^{-1}$ h^{-1} in October and April respectively. Isoprene emission factor increased significantly by a factor of 2 in August and September under AD (137.8 and 74.3 µgC g$_{DM}$$^{-1}$ h^{-1}) compared ~~to ND (75.3 and 40.21 µgC g~~$_{DM}$$^{-1}$ ~~h~~$^{-1}$~~), but no changes occurred on ER.~~with ND (75.3 and 40.21 µgC g$_{DM}$$^{-1}$ h^{-1}), but no significant changes occurred on ER. Aside from the June 2012 & 2013 measurements, MEGAN2.1 model was able to assess the observed ER variability only when its soil moisture activity factor γ_{SM} was not operating, and regardless of the drought intensity; in this case more

Style Definition: Heading 1: Font color: Text 1, Do not check spelling or grammar, Line spacing: single, Outline numbered + Level: 1 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0 cm + Indent at: 0.76 cm

Style Definition: Heading 2: Font color: Text 1, Outline numbered + Level: 2 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0 cm + Indent at: 1.02 cm

Style Definition: Heading 3: Outline numbered + Level: 3 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0 cm + Indent at: 1.27 cm

Style Definition: Comment Text

Style Definition: titre 22: Indent: Left: 2.5 cm, First line: 1.25 cm, Outline numbered + Level: 2 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0 cm + Indent at: 1.02 cm

Formatted: Font: 16 pt

Formatted: Left, Space After: 10 pt, Line spacing: Multiple 1.15 li, Tab stops: Not at 19.39 cm + 21 cm + 22.62 cm + 24.23 cm + 25.85 cm

Formatted: Font: 16 pt, Not Bold

Formatted: Font: 16 pt, Not Bold

Formatted: Font: 16 pt, Not Bold

Formatted: Font: 16 pt, Not Bold

Formatted: English (U.K.)

Formatted: English (U.K.)

Formatted: Hyperlink, Font: 12 pt, English (U.K.)

Formatted: Space Before: 6 pt, After: 18 pt

Formatted: Font: 16 pt

than 80% and 50% of ER seasonal variability was assessed in the ND and AD respectively. We suggest that a specific formulation of γ_{SM} be developed for drought adapted isoprene emitter, according with that obtained for *Q. pubescens* in this study ($\gamma_{SM} = 0.192e^{51.93\ SW}$, with SW the soil water content). An isoprene algorithm (*G*14) was developed using an optimised artificial neural network trained on our experimental dataset (ER + O_3HP climatic and edaphic parameters cumulated over 0 to 21 days ~~before~~prior to the measurements). *G*14 assessed more than 80% of the observed ER seasonal variations, whatever the drought intensity. ~~In contrast, ER was poorly assessed under water stress by MEGAN empirical isoprene model, in particular under AD. Soil water (SW) content was the dominant parameter to account for the observed ER variations, regardless the water stress treatment. ER~~ER$_{G14}$ was more sensitive to higher (0 to -7 days) frequency environmental changes under AD ~~(0 to -7 days) compared~~in comparison to ND~~ (7 days).~~. Using IPCC RCP2.6 and RCP8.5 climate scenarios, and SW and temperature as calculated by the ORCHIDEE land surface model, ~~and *G*14, an annual 3 fold ER relative increase~~ ER$_{G14}$ was found ~~between present (2000-2010) and future (2090-2100) for RCP8.5 scenario compared to a 70% increase for RCP2.6. Future ER remained mainly~~to be mostly sensitive to ~~SW (both scenarios)~~future temperature, and nearly not to precipitation decrease (an annual increase of up to 240% and ~~became dependent to higher frequency environmental changes under RCP8.5~~at the most 10% respectively in the most severe scenario). The main impact of future drier conditions in the Mediterranean was found to be an enhancement (+40%) of isoprene emissions sensitivity to thermal stress.

1 ~~1.~~ Introduction

A large number of Mediterranean deciduous and evergreen ~~tree species~~trees produce and release isoprene (2-methyl-1,3-butadiene, C_5H_8). Under non~~-~~-stress conditions, only 1-2% of the carbon recently assimilated is emitted as isoprene, ~~while,~~whereas under stress conditions such as water scarcity~~,~~ this value can reach up to 20-30% (~~*Q.*~~*Quercus* *pubescens*, Genard-Zielinski et al., 2014). Although the role of isoprene ~~is still under discussion~~remains a subject of debate, it seems likely that C_5H_8 helps plants to optimise CO_2 assimilation during temporary and mild stresses, especially during the growing and warmer periods (~~Loreto &~~Brili et al., 2007Loreto and Fineschi, 2015). The major role of isoprene in plant defence probably explains its large annual global emissions (440-660 TgC.y^{-1}, Guenther et al., 2006), forming the largest quantity of all Biogenic Volatile Organic Compounds (BVOC) emitted. Although present in the atmosphere at the ppb or ppt level, isoprene has a broad impact on

Formatted: Heading 1, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

Formatted: English (U.K.)

Formatted: Font: Italic

Formatted: Font: Italic

atmospheric chemistry, both in the ~~gaz~~gas phase (especially in the O_3 budget of some urbanised areas, Atkinson and Arey, 2003) and in the particulate-phase (secondary organic aerosols formation~~)~~, ~~(~~Goldstein ~~&~~and Steiner, 2007)~~, hence on the biosphere-atmosphere feedbacks~~, and hence on biosphere-atmosphere feedbacks. For instance, in the Mediterranean area, Curci et al. (2009) showed that isoprene could be responsible for the production of 4 to 6 ppbv of ozone between June and August, representing 16-20% of total ozone. Given the broad impacts of isoprene on atmospheric chemistry, considerable efforts have been made to (i) understand the physiological mechanisms responsible for isoprene synthesis and emission and the different environmental parameters that control their variability, in order to (ii) develop isoprene emission models that can account for the broadest possible range of environmental conditions.

~~It~~Thus, it has extensively been shown that~~,~~ under non-stressful conditions, isoprene synthesis and emission are ~~tightly linked,~~closely connected and ~~mainly dependent on the mere instantaneous~~primarily depend upon light and temperature conditions (Guenther et al., 1991, 1993). ~~By~~In contrast, under environmental stress, isoprene emission and synthesis are uncoupled ~~under stress environmental conditions which influence isoprene emissions~~ in a way that is not ~~completely~~fully understood and hence still under debate (Affek ~~&~~and Yakir, 2003; Peñuelas ~~&~~and Staudt, 2010). ~~Whilst~~Indeed, although some authors ~~highlighted~~have identified an increase in isoprene emission ~~increase~~ under mild water stress (Sharkey ~~&~~and Loreto, 1993; Funk et al., 2004; Pegoraro et al., 2004; Genard-Zielinski et al., 2014)~~, other studies report~~, others have reported the opposite (Bruggemann ~~&~~and Schnitzler, 2002; Rodriguez-Calcerrada et al., 2013; Tani et al., 2011)~~. Furthermore, isoprene emission intensity is also closely related to plant internal factors such as leaf ontogeny in deciduous species. The capacity of young leaves to release isoprene only occurs when a cumulated temperature threshold (degree day) is reached after bud breaking (Grinspoon *et al.*, 1991). Depending on the emitter and the location, this threshold was observed to range from 120 to 210 °C (*Salix phylicipholia*, Hakola *et al.*, 1998) to 400 °C (*Populus tremuloides*, Monson *et al.*, 1994). Moreover, after the emission onset, the seasonal variations of the leaf capacity to emit isoprene which can range over several orders of magnitude along the season (Monson *et al.*, 1994, Geron *et al.*, 2000; Boissard *et al.*, 2001; Petron *et al.*, 2001; Hakola *et al.*, 1998).~~. ~~Two~~Concerning the modelling of isoprene emission variations, two main approaches have been considered so far~~ to model isoprene emission variations:~~: (i) empirically~~-~~ based parameterisations to represent ~~the~~ observed emission variations ~~due~~in relation to easily accessible environmental drivers, and (ii) process-based relationships built on ~~our~~the

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Spanish (Spain-Traditional Sort)

Formatted: Spanish (Spain-Traditional Sort)

Formatted: Font: Italic, Spanish (Spain-Traditional Sort)

Formatted: Spanish (Spain-Traditional Sort) understanding of the ongoing biological regulation (see Ashworth et al., 2013). ~~Although both~~Both types of model are adapted for ~~present day~~ global/regional modelling, ~~only~~but the former ~~ones~~ are more commonly used for atmospheric applications, especially for air quality exercises for which mechanistic models ~~are~~remain far too complex. ~~Although~~Indeed, whilst Grote et al. (2014) ~~showed the ability of~~have indicated that such models ~~to account~~are fairly ~~well~~effective in accounting for the mild stress effects on seasonal isoprene variations of *Quercus*~~.~~ *ilex*~~.,~~, the ~~high degree~~large number of necessary descripting parameters ~~required still~~ continues to represent an obstacle for their broad and routine use in air quality ~~and global scale emission exercises~~ (Ashworth et al., 2013). ~~On the other hand, because~~Moreover, the ~~more~~development of BVOC empirical emission models, and especially of the most widely used empirical ~~models (see~~model, MEGAN~~:~~ (Model of Emissions of Gases and Aerosols from Nature, Guenther et al., 2006~~) were developed using~~ , 2012), was partly based on measurements ~~made~~carried out under 'optimum' growing conditions~~, it is still necessary to broaden their ability to assess isoprene emissions over a larger~~ and/or obtained from very few emitters. Therefore, if they depict a fair picture of the general level and global distribution of BVOC emission, they remain somewhat deficient in accounting for a large range of stress conditions. When used for air quality monitoring applications, such a bias intrinsic to the model can significantly weaken air quality forecasts in areas that are greatly influenced by biogenic sources (von Kuhlmann et al., 2004; Chaxel and Chollet, 2009). Concerning the impact of drought strees, the inclusion of the soil moisture effect on isoprene emission in MEGAN was derived from a sole drought study made on *Populus deltoides* (Pegoraro et al., 2004). Validation regarding a broader range of environmental conditions (including stress conditions) and ~~variation frequencies (from high or instantaneous to low or seasonal). Such improvements imply ongoing updates as research studies go along and thereby require more advanced algorithms. In particular, MEGAN model is still struggling in considering the water availability (from precipitation or present in the soil) effects on isoprene emissions. Such a weakness~~ emitters is necessary. Weaknesses in accounting for the impact of drought can be ~~particularly~~ detrimental to isoprene emission inventories~~ made over~~, especially when undertaken in areas that are covered with a large quantity of high isoprene emitters and that are subject to frequent drought episodes, like the Mediterranean region. ~~Besides~~Moreover, in addition to a predicted temperature increase of between 1.5 and 3°C, climate models ~~predict~~ over this area predict an amplification of the natural drought during summers due to a ~~precipitation~~ reduction ~~which~~ in precipitation that could~~,~~ locally~~,~~ reach up to 30% by the year 2100 (Giorgi ~~&~~and Lionello, 2008; ~~IPCC~~ Intergovernmental Panel on Climate Change, 2013;

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Not Italic, English (U.S.)

Polade et al~~.~~., 2014). ~~Due~~Owing to the ~~strong~~close interactions ~~existing~~ between air pollution over ~~the~~ large Mediterranean urban areas and strong BVOC emissions ~~by local~~from nearby vegetation, the ~~assessement~~potential impacts of ~~how global~~future climatic changes ~~could impact~~on isoprene emissions ~~is a growing~~represents an acute environmental issue needing to be ~~adressed~~addressed (Chameides et al., 1988; Atkinson ~~&~~and Arey, 1998; Calfapietra et al., 2009; ~~Chameides *et al*., 1988;~~ Pacifico et al~~.~~., 2009). ~~In that~~Within this context, a recent study ~~underlines~~has underlined the importance of monitoring over a long~~-term monitorings of,~~ period both~~,~~ isoprene emissions and soil moisture in water limited ecosystems (Zheng et al., 2015). Since ~~*Quercus*~~Q. *pubescens* Willd. is the second largest isoprene emitter in Europe (and ~~the main one~~foremost in the Mediterranean zone) (Keenan et al~~.~~., 2009), it represents an ideal model species by which to~~ further~~ investigate ~~the~~ isoprene emission variability under drought conditions.

The objectives of this study were ~~to~~ (i) ~~compare observed seasonal impacts~~to investigate *in natura* the influence of natural (ND~~ *vs* ~~) and amplified (AD) drought on *Q.* ~~*pubescens* gaz~~*Pubescens* seasonal gas exchanges (CO_2, H_2O~~)~~), and in particular, isoprene emission rates (ER~~) at the O_3HP site, (ii) develop a specific isoprene emission algorithm taking into account drought (ND and AD) impacts on *Q. pubescens*~~); (ii) to test and compare two empirical emission models, MEGAN2.1 (Guenther et al., 2012) and *G*14 (this study), in assessing seasonal ER~~, and,~~ variability under different drought intensities, and (iii) ~~make some projections on the impacts of an AD of 30% on Downy oak~~to evaluate the sensitivity of ER ~~over the Mediterranean area by the year 2100, under IPCC~~to future climatic changes (warming and precipitation reduction) based on two extreme IPCC scenarios: RCP2.6 (moderate) and RCP8.5 (extreme~~) scenarios.~~).

2 ~~2.~~ Materials and methods

2.1 ~~2.1~~ Experimental site O_3HP

Experimental data ~~was~~were obtained at the O_3HP site (Oak Observatory at the Observatoire de Haute Provence, 5°42'44" E, 43°55'54" N). This site ~~is~~constitutes part of the French national network SOERE F-ORE-T (System of Observation and Experimentation, in the long term, for Environmental Research) ~~dedicate~~dedicated to investigating the functioning of the forest ecosystem~~ functioning~~. The O_3HP site (680 m above mean sea level) is located 60 km north of Marseille and consists of a homogeneous 70-100 year-old ~~forest~~coppice dominated

Formatted: Font: Not Italic

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: Font: Italic, English (U.S.)

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: Font: Italic

Formatted: Font: Not Italic

Formatted: Font color: Auto, English (U.S.)

Formatted: Font color: Auto, English (U.S.)

Formatted: Font color: Auto, English (U.S.)

Formatted: Font color: Auto, English (U.S.)

Formatted: Font color: Text 1

Formatted: Line spacing: single

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

by *Q. pubescens* (5 m in height~~,~~; Leaf Area Index LAI = 2.2~~)~~), which accounts for ≈ 90% of the biomass and ≈75% of the trees. ~~O_3HP facilities, in particular the rain exclusion system~~A rainout-shelter above 300 m^2 of the canopy dynamically ~~reducing~~removed any precipitation (rain, snow and hail) by ~~a deployable roof above~~ deploying automated shutters. This facility facilitated the ~~canopy, enabled to~~ study ~~this ecosystem~~of *Q. pubescens* under natural and amplified drought ~~(averaging -30% of the annual cumulated precipitation), hereafter named~~, henceforth referred to as 'ND' and 'AD' plot respectively. In the present study, the device was deployed during rain events from the end of May until October 2012 in order to exclude 32% of the precipitation in the rain exclusion plot. In practice, almost all rainfall in late spring and summer was thus intercepted. This percentage corresponds with the highest IPCC projections made for the end of the century over the Mediterranean area, and accords with the precipitation reduction at O_3HP during the driest years from 1967 to 2000 compared with the average precipitation over this period. Using an ombrothermic diagram ($P<2T$, with P=monthly precipitation in mm, and T=monthly air temperature in °C), we assessed that the summer 2012 drought period reaches 4.5 months in the AD plot, compared with 3 months in the ND plot. Ambient and soil environmental parameters were continuously monitored ~~with~~using a dense network of sensors (for details see ~~section "COOPERATE environmental data base").~~Section 2.7). Access to the canopy was at two levels: ≈ 0.8 and ~~4~~3.5 m (top canopy branches) above ground level, with the ~~higher~~highest level being the ~~focus of~~ one at which we undertook this study. Further description can be found in ~~(~~Santonja et al. (2015).

2.2 ~~2.2~~ Seasonal sampling strategy

Isoprene emission rate measurements were ~~performed~~ undertaken for at least ~~during~~ one week~~, once a~~ per month~~,~~ from June 2012 to June 2013, except for the period from November 2012 ~~to~~until March 2013 when *Q. pubescent* is fully senescent with leaves remaining on the tree (marcescent species). This calendar ~~allowed~~enabled us to capture isoprene emissions during leaf maturity but also during bud break (April 2013) and just before leaf senescence (October 2012). Three trees were studied in each plot along the whole seasonal cycle, with a single branch at the top of the canopy ~~being mostly~~predominantly sampled for each tree. More intensive measurements were carried out in June 2012 (3 weeks) and April 2013 when tree-to-tree and within-canopy variability was assessed. One ND branch was subsequently sampled throughout all intensive campaigns, ~~while~~and the ~~5~~five other ND and AD branches were ~~alternatively~~alternately sampled during ~~1~~for one to ~~2~~two days ~~(Genard-Zielinski *et al.*,~~

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1, English (U.S.)

Formatted: Font color: Text 1, English (U.S.)

Formatted: Font color: Text 1, English (U.S.)

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

~~2014).~~(Genard-Zielinski et al., 2015). Isoprene samples were collected on cartridges packed with adsorbents, ~~except~~apart from in April 2013 ~~where on-line~~when online isoprene measurements were ~~performed~~conducted using a PTR-MS directly connected to the enclosure via a 50~~-~~ m ~~length~~ 1/4” PTFE line. When cartridges were used, samples (volume ranging between 0.45 L and 0.9 L, depending on the expected emission intensity) were taken from sunrise to sunset, roughly every ~~2~~two hours. PTR-MS measurements allowed a higher sampling frequency (between 120~~ and ~~-390 s^{-1}).

Branch enclosures were ~~mostly~~generally installed on the ~~previous~~ day before the first emission rate measurement ~~took place~~was taken, and~~,~~ at least~~, 2 h before.~~

~~1.1~~ ~~2.3~~ two hours beforehand in order for~~COOPERATE environmental database~~

~~Ambient and edaphic parameters used for the artificial neural network (ANN) optimization were obtained from the COOPERATE database (https://cooperate.obs-hp.fr/db) and daily averaged for each day of our study. Ambient PAR (µmol~~ $\sout{m^{-2}}$ $\sout{s^{-1}}$~~) measured above the canopy at 6.5 m (Licor Li-190®; Lincoln, NE, USA) in the ND plot was used as the PAR reaching all~~ the ~~top canopy~~plant to return to normal physiological functioning. Note that although senescence had just begun in October 2012, we did check that the enclosed branches ~~studied. Ambient air temperature (*T*, °C) measured at 6.15 m (multisensor Vaisalla) in the ND and AD plot was used for both sets of branches. Since some precipitation (*P*, mm) values~~ were ~~missing from the COOPORATE database during our data processing, P values from the nearby (< 10 km) Forcalquier meteorological station were used. Soil water content (SW, L L~~$\sout{^{-1}}$~~) and temperature (ST, °C) at -0.1 m (Hydra Probe II SDI-12, Stevens, Water Monitoring Systems Inc., OR, USA) specific for each of the sampled trees were selected and extracted from the COOPORATE database. When data were missing, they were extrapolated from the nearest equivalent data point~~not senescent during these measurements.~~ Daily mean PAR, *T*, *P*, SW and ST were cumulated over a time period ranging from 1 to 21 days before the measurement~~

2.3 ~~2.4~~ Branch scale isoprene emissions and gas exchanges

~~Sampling was carried out using two identical dynamic branch enclosures (detailed description in Genard-Zielinski *et al.*, 2014). Briefly, the device consists of a ≈ 60 L PTFE (PolyTetraFluoroEthylene) frame closed by a sealed 50 µm thick PTFE film to which ambient~~

Formatted: Heading 2, Left, None, Space Before: 0 pt, After: 0 pt, Line spacing: single, Don't keep with next, Don't keep lines together, Pattern: Clear, Tab stops: Not at 19.39 cm + 21 cm + 22.62 cm + 24.23 cm + 25.85 cm

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1

Formatted: Font color: Auto

Formatted: English (U.S.)

Formatted: Font color: Auto

Formatted: English (U.S.)

Formatted: Font color: Text 1

~~air was introduced at Q_0 ranging between 11–14~~ Sampling was undertaken using two identical dynamic branch enclosures (detailed description in Genard-Zielinski et al., 2015). Briefly, the device consisted of a ≈ 60 L PTFE (PolyTetraFluoroEthylene) frame closed by a sealed, 50 µm-thick PTFE film, to which ambient air was introduced at Q_0 ranging between 11–14 L min^{-1} using a PTFE pump (KNF N840.1.2FT.18®, Germany). Gas flow rates were controlled by mass flow controllers (Bronkhorst) and all tubing lines were PTFE-made. A PTFE propeller ensured ~~a~~the rapid mixing of air inside the chamber. ~~Microclimate~~The microclimate (PAR, *T*, relative humidity) inside the chamber was continuously monitored (relative humidity and temperature probe LI-COR 1400–04®, and quantum sensor LI-COR, PAR-SA 190®, Lincoln, NE, USA) and recorded (Licor 1400®; Lincoln, NE, USA). CO_2/H_2O exchanges from the enclosed branches were also continuously measured using infrared gas analysers (IRGA 840A®, Licor) in order to assess the net assimilation P_n (in µmol$_{CO2}$ m^{-2} s^{-1}) and the stomatal conductance to water vapour G_w (mol$_{H2O}$ m^{-2} s^{-1}) using the equations from Von Caemmerer ~~& Farquhar (1981) as detailed in Genard-Zielinski *et al.* (2015).~~and Farquhar (1981) as detailed in Genard-Zielinski et al. (2015).

Total dry biomass matter (DM) was calculated by manually scanning every leaf of each sampled branch enclosed in the chamber and applying a dry leaf mass per area conversion factor (LMA) extrapolated from concomitant measurements made on the same site. ~~Mean~~The mean (range) DM was 0.16 (0.01 - 0.45) g$_{DM}$, and mean (range) ~~AF~~LMA was 13.17 (0.82 - 36.67) g$_{DM}$ cm^{-2}.

Isoprene emission rates (ER) were calculated as:

$$ER = Q_0 \times (C_{out} - C_{in}) \times DM^{-1}, \tag{1}$$

Formatted: Tab stops: 15.75 cm, Right + Not at 15 cm

Formatted: Font: Not Italic

where ER is expressed in µgC g$_{DM}^{-1}$ h^{-1}, Q_0 is the flow rate of the air introduced into the chamber (L h^{-1}), ~~C_{out}~~C_{in} and ~~C_{in}~~C_{out} are the concentrations in the inflowing and outflowing air (µgC L^{-1}~~)~~), and DM is the sampled dry biomass matter (g$_{DM}$).

Formatted: Font: Not Italic

~~All over~~Throughout the seasonal cycle, except in April, isoprene was collected using packed cartridges (glass and stainless-steel) prefilled with Tenax TA and/or Carbotrap. Isoprene was then analysed in the laboratory according to a gas chromatography–mass spectrometry (GM-MS) procedure detailed in ~~(Genard-Zielinski *et al.*, 2014),~~Genard-Zielinski et al. (2015), with a level of analytical precision ~~better~~greater than 7.5%.

In April 2013, ~~additionally to cartridges,~~ two types of PTR-MS were used for ~~on-line~~online isoprene sampling and analysis. A quadrupole PTR-MS (HS-PTR-MS, Ionicon Analytik GmbH, Innsbruck Austria), connected to the ND branch enclosure, was operated at 2.2 mbar pressure, 60°C temperature and~~ a~~ 500 V voltage in order to achieve an E/N ratio of ≈ 115 Td (E: electric field strength (V cm^{-1}); N: buffer gas number density (molecule cm^{-3}); 1Td=10^{-17} V cm^{2}. The primary H_3O^+ ion count assessed at *m/z* 21 was 3 10^{7} cps, with a typically < 10% contribution monitored from the first water cluster (*m/z* 37) and < 5% contribution from the O_2^+ (*m/z* 32). Measurements were operated in scan mode (*m/z* 21 to *m/z* 210) every 380 s. After 15~~ to ~~-20 min of sampling of incoming air, the outgoing air was sampled for 30 to 60 min. A high resolution (m/Δm ≈ 4000) time of flight PTR-MS (PTR-ToF-MS-8000, Ionicon Analytik GmbH, Innsbruck Austria) connected to the second enclosure used in our study enabled us to discriminate compounds when their masses differ at the tenth part. The main experimental characteristics were similar to the PTR-MS-Quad, but a ~~550 V~~ voltage of 550 V was used in order to reach an E/N ratio of ≈ 125 Td. The H_3O^+ ion count assessed at *m/z* 21 was 1.1 10^{6} cps with a similar < 10% contribution monitored from the first water cluster (m/Z 37) and < 2.5% contribution from the O_2^+ (*m/z* 32). The signal at m/z 69 corresponding to protonated isoprene was converted into mixing ratio by using a proton transfer rate constant k of 1.96.10^{-9} cm^{3}.s^{-1} (Cappellin et al., 2012), the reaction time in the drift tube, and the experimentally determined ion transmission efficiency. The relative ion transmission efficiencies of both instruments were assessed using a standard gas calibration mixture (TO-14A Aromatic Mix, Restek Corporation, Bellefonte, USA; 100 ± ~~10ppb~~10 ppb in nitrogen). Assuming an uncertainty of ±15% in the k-rate constants and in the mass transmission efficiency, the overall uncertainty of the concentration measurement is estimated to be of the order of ±20%. Background signal was obtained by passing air through a platinum catalytic converter heated at 300°C. Detection limits defined as three times the standard deviation on the background signal were 10 and 50 ppt with the PTR-ToF-MS and the HS-PTR-MS respectively. An intercomparison between both the cartridge+GC-MS and PTR-MS protocols was undertaken parallel with another emitter present on the site (*Acer monspessulanum*); no significant difference was observed between the techniques (Genard-Zielinski et al., 2015). The overall uncertainty (sampling + analysis) on ER assessment was between ~~15~~20% and ~~20~~25%.

2.4 ~~2.5~~ Statistics

All statistics were performed on STATGRAPHICS® centurion XV by Statpoint, Inc. ~~Isoprene emission factors (I_s) under each plot were calculated as the slope of the linear regression between C_L × C_T (factors accounting for light and temperature variability of~~

Formatted: Font: Italic

Formatted: Font color: Text 1

Formatted: Font color: Text 1, English (U.K.)

Formatted: Heading 2, Left, None, Space Before: 0 pt, After: 0 pt, Line spacing: single, Don't keep with next, Don't keep lines together, Pattern: Clear, Tab stops: Not at 19.39 cm + 21 cm + 22.62 cm + 24.23 cm + 25.85 cm

Formatted: Font color: Text 1

Formatted: Font: Not Bold, Font color: Text 1

~~isoprene emissions respectively, as in Guenther *et al.*, 1993) and measured ER, with the exception of July when no such correlation was found (cf. Results). $C_L \times C_T$ were calculated using PAR and *T* recorded in the enclosure.~~ Differences in P_n, G_w, ER and ~~I_s~~$\varepsilon_{iso,Qp}$ between the ND and the AD plot were tested using ~~U-~~Mann~~ &~~ -Whitney U-tests~~).~~. Seasonal changes in these ecophysiological parameters were tested using the Krusal-wallis test (K) and the analysis was performed separately on trees from the ND and AD plot. Comparisons between ~~COOPORATE~~COOPERATE environmental data (see Section 2.7) were made using a Wilcoxon test when data ~~was~~were not log-normal, and a *t*-test when log-normal.

2.5 Branch scale ER assessment using MEGAN2.1 emission model

Based on the latest version of the MEGAN model (MEGAN2.1, Guenther et al., 2012), *Q. pubescens* ER were assessed for the sampling conditions of our seasonal study using:

$$ER_{MEGAN} = \varepsilon_{iso,Qp}\ \chi_{Qp}\ \gamma_{iso} \qquad (2)$$

where :

- $\varepsilon_{iso,Qp}$ is the *Q. pubescens* isoprene emission factor calculated under each plot, every month of our study, as the slope of the linear regression between ER and $C_L \times C_L$ (see Section 3.2; in µgC g_{DM}^{-1} h^{-1}), where C_L and C_L are the instantaneous response of isoprene emissions to PPFD and T deviations to standard conditions (1000 µmol m^{-2} s^{-1} and 30°C respectively) (Guenther et al., 1995); $C_L \times C_T$ were calculated using PAR and *T* recorded in the enclosure.

- χ_{Qp} is the fractional grid areal coverage taken equal to 1 since only *Q. pubescens* emissions (100%) were considered;

- and γ_{iso} is the isoprene emission activity factor defined as:

$$\gamma_{iso} = \gamma_P\ \gamma_T\ \gamma_A\ \gamma_{SM}\ \gamma_C \qquad (3)$$

where:

- γ_P and γ_T are the isoprene empirical responses to light and temperature respectively, using instantaneous, daily and 10 days PPFD and T values (for details see Guenther et al., 2012);

- γ_A is the age emission activity based on empirical coefficients applied on new (0.05 applied for all April measurements), growing (0.6 for June) mature (1 for July and August) and old (0.6 for September and October) leaves;

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font: Not Bold, Font color: Text 1, English (U.K.)

- γ_{SM}, is the soil moisture dependence of isoprene emissions according to soil moisture value (θ, m^3 m^{-3}) based on the Pegoraro et al. (2004) drought study on *Populus deltoides*:

$$\gamma_{SM} = 1 \qquad \text{for } \theta > \theta_1 \qquad (4a)$$

$$\gamma_{SM} = (\theta-\theta_w)/\Delta\theta_1 \qquad \text{for } \theta_w < \theta < \theta_1 \qquad (4b)$$

$$\gamma_{SM} = 0 \qquad \text{for } \theta_w < \theta_1 \qquad (4c)$$

where θ_w is the wilting point (the soil moisture below which plants cannot extract water from soil, m^3 m^{-3}), $\Delta\theta_1 = 0.014$ is an empirical parameter, and $\theta_1 = \theta_w + \Delta\theta_1$. θ_w was assessed to be 0.15 m^3 m^{-3} at the O_3HP, a value very close to the 0.138 m^3 m^{-3} value given by Chen and Dudhia (2001) for clay and sand soil found at the O_3HP;

- and γ_C is the CO_2 inhibition, set to 1 here as no CO_2 effect was tested in our study.

NB: in order to be comparable with our measurements carried out on top canopy leaves and expressed as net emission rates in the unit of µgC g_{DM}^{-1} h^{-1}, no canopy environment coefficient C_{CE} nor LAI was considered in the calculation of γ_{iso}, and thus in ER_{MEGAN} (for further details see Guenther et al., 2012).

2.6 Branch scale ER assessment using an Artificial Neural Network ~~(ANN)~~trained on field data

The Artificial Neural Network (ANN) developed in this study to assess branch scale ER from *Q. pubescens* (henceforth referred to as *G14*) was based on a commercial version of the Netral NeuroOne software v.6.0 ~~(http://www.netral.com,~~(inmodelia.com, France~~)~~). The ANN was used as a Multi-Layer Perceptron (MLP) in order to calculate multiple non-linear regressions between a set of input regressors x_i (the environmental variables measured at the O_3HP) and the output data ~~y_{meas}~~ (the measured isoprene ER). The assessed ER (~~y_{calc}~~ER_{G14}) was calculated as follows:

$$\cancel{y_{calc}}ER_{G14} = w_0 + \sum_{j=1}^{j=N}\left[w_{j,k} \times f\left(w_{0,j} + \sum_{i=1}^{i=n} w_{i,j} \times x_i\right)\right], \qquad (\cancel{2}5)$$

where w_0 is the connecting weight between the bias and the output, N the number of neurons N_j, f the transfer function, $w_{0,j}$ the connecting weight between the bias and the neuron N_j, w_i the connecting weight between the input and the neuron N_j, and x_i the n input regressors. The MLP optimisation of the weights w was achieved according to Boissard et al~~.,~~. (2008). Every

Formatted: Heading 2, Left, None, Space Before: 0 pt, After: 0 pt, Line spacing: single, Don't keep with next, Don't keep lines together, Pattern: Clear, Tab stops: Not at 19.39 cm + 21 cm + 22.62 cm + 24.23 cm + 25.85 cm

Formatted: Font color: Text 1

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Tab stops: 15.75 cm, Right + Not at 15 cm

Formatted: Font: Italic

input regressor x_i was centrally-normalised. Two sub-datasets were considered, for the ND and AD plot respectively. For each sub-dataset, 80% of our data were used for training and optimising the MLP, and the ~~overall~~remaining 20% were used for blind validation based on root mean square error (RMSE). Training/validation splitting was made using a Kullback-Liebler distance function available in NeuroOne v 6.0. Only the nonlinear hyperbolic tangent (*tanh*) function was tested as transfer function *f*. Up to N=7 neurons were tested for every ANN setting. Overtraining phenomenon (a too large number of neurons *vs* the number of input parameters) was checked against the $\mathrm{RMSE}_{\mathrm{training}}/\mathrm{RMSE}_{\mathrm{validation}}$ evolution *vs* the number N of neurons tested.

Among the other available statistical methods, ANNs present the advantage of being the most parsimonious, i.e., giving the smallest error for a same number of descriptors (see for instance Dreyfus et al., 2002). Moreover, the ANN approach, as is the case of other non-linear regression methods, is not particularly sensitive to regressors’ co-linearity (Bishop, 1995; Dreyfus et al., 2002). On the other hand, one of the limitations of ANNs is that they can only be employed for interpolation within the range of values of the trained data, and not for extrapolation exercises beyond this range. Consequently, during the isoprene emission sensitivity to future climatic changes (see Section 2.8), only x_i values fitting within the range of variation tested during the training phase were considered; in total 21% of the data were thus rejected.

2.7 COOPERATE environmental database

Ambient and edaphic parameters used for the ANN optimization were obtained from the COOPERATE database (https://cooperate.obs-hp.fr/db) and daily averaged for each day of our study. Ambient PAR (µmol m^{-2} s^{-1}) measured above the canopy at 6.5 m (Licor Li-190®; Lincoln, NE, USA) in the ND plot was used as the PAR reaching all of the top canopy branches studied. Ambient air temperature (*T*, °C) measured at 6.15 m (multisensor Vaisalla) in the ND and AD plot was used for both sets of branches. Since some precipitation (*P*, mm) values were missing (<5%) from the COOPERATE database during our data processing, *P* values from the nearby (< 10 km) Forcalquier meteorological station were used. The bias between cumulated *P* (P_{cum}) curves at both sites was assessed and considered in order to extrapolate the missing values at the O$_3$HP site. As *P* was cumulated over 7, 14 and 21 days, the resulting bias was negligible (≈ 1%) and no further adjustment was made. Soil water content (SW, L L^{-1}) and temperature (ST, °C) at -0.1 m (Hydra Probe II SDI-12, Stevens, Water Monitoring Systems Inc., ~~**2.7 Future climate data over the Mediterranean area and ORCHIDEE model description**~~

~~For the present-day climate, *T*, *P* and PAR~~OR, USA) specific to each of the sampled trees were selected and extracted from the COOPERATE database; when soil data were missing, they were extrapolated from the nearest equivalent data point measurement. Daily mean PAR, *T*, *P*, SW and ST were cumulated over a time period ranging from 1 to 21 days before the measurement.

2.8 ORCHIDEE land surface model: providing future conditions to investigate ER sensitivity to climatic changes

Present-day *T* and *P* were assessed as the 2000-2010 daily averages~~ and~~ derived from the ISI–MIP (Inter-Sectoral Impact Model Intercomparison Project) climate data set (Warszawski et al., 2014) over the Mediterranean area~~ which~~. This data set contains the bias-corrected daily simulation ~~output~~outputs of the earth system model HadGEM2-ES. ~~The corresponding data~~ Corresponding values for the 2090-2100 period were used to assess the expected range of future climatic changes. They were derived from two ISI–MIP future projections forced along two Representative Concentration Pathways (RCPs): the so-called ‘peak-and-decline’ greenhouse gas concentration scenario RCP2.6 (optimistic or moderate scenario~~)~~), and the

Formatted: Font color: Text 1

Formatted: Heading 2, Left, None, Space Before: 0 pt, After: 0 pt, Line spacing: single, Don't keep with next, Don't keep lines together, Pattern: Clear, Tab stops: Not at 19.39 cm + 21 cm + 22.62 cm + 24.23 cm + 25.85 cm

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Auto

Formatted: Font color: Auto

Formatted: Font: Not Italic

Formatted: Font: Not Italic

'rising' greenhouse gas concentration scenario RCP8.5 (extreme or severe scenario). All T~~, P~~ and ~~PAR~~P data were extracted for the entire Mediterranean region from the global ISI-MIP data set and subsequently averaged over the area.

Using these present and future T, P and PAR values (ISI-MIP derived), the corresponding present and future SW and ST were assessed by running the global land-surface-model ORCHIDEE (ORganizing Carbon and Hydrology In Dynamic EcosystEms) over the European part of the Mediterranean region. ~~Calculated~~ The calculated SW and ST were averaged over this area. ORCHIDEE is a spatially explicit, process-based model ~~calculating~~that calculates the CO_2, H_2O~~,~~ and heat fluxes ~~exchanged~~ between the land surface and the atmosphere. ~~The processes~~Vegetation species distributed at the Earth's surface are represented in ORCHIDEE through 13 Plant Functional Types (PFTs). Processes in the model are represented at the time step of ½ hour~~ basis~~, but the variations of water and carbon pools are calculated on a daily basis. ~~Vegetation is described using 12 Plant Functional Types (PFT). Each PFT follows the same set of governing equations but takes different parameter values, except for the leafy season onset and offset, which are defined by PFT specific equations.~~ A detailed description of ~~the model~~ORCHIDEE is ~~given in~~provided by Krinner et al. (2005). Simulations over the European part of the Mediterranean region were performed with the ORCHIDEE model at 0.5 × 0.5° spatial resolution~~,~~ using the soil parameters (clay, silt and sand fractions) from Zobler (1986~~) and since~~). Given that this study focuses on isoprene emissions from *Q. pubescens*, we fixed the vegetation with the corresponding PFT 'temperate broad-leaf summer green tree'. The ~~above~~ described ISI-MIP historical forcings and the ISI-MIP future projections were used as climate ~~data~~conditions for ORCHIDEE runs and ER assessment using *G*14. Equilibrium was reached by running ORCHIDEE on the first decade of the climate forcing (1961-1990) repeated in a loop, and the value of atmospheric CO_2 corresponding to the year 1961. Among the two different hydrology schemes available in ORCHIDEE, the~~ rather complex~~ physically based 11-layer scheme was used (Guimberteau et al., 2013).

~~3.~~ ER sensitivity to moderate and severe temperature and/or precipitation changes was evaluated using *G*14 under 6 cases: (i) the 'T' (respectively, 'P') test was conducted considering only T and ST (respectively, only P and SW) changes according to RCP2.6 scenario; (ii) the 'TT' and 'PP' tests were similar to the 'T' and 'P' tests but considered changes according to RCP8.5 scenario; (iii) the 'T+P' (respectively, 'TT+PP') test combined the effect of T, ST, P and SW changes according to RCP2.6 (respectively, RCP8.5).

Formatted: Font: Italic

Formatted: Font: Not Italic

Formatted: Line spacing: single

3 Results

Formatted: Heading 2, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

3.1 ~~3.1~~ Environmental conditions observed at the O_3HP

Mean daily ambient air temperature *T* varied between -3 and 26~~-~~°C (January 2013 and August 2012 respectively, Fig. 1a). Seasonal PAR variations were in line with *T* variations, with the daily ~~means~~mean peaking at 900 µmol m^{-2} s^{-1} in July (Fig. 1b). In 2012, the amplification of the ND was adjusted from May to reach its maximum (32%) in July and maintained until November when rain exclusion was stopped (Fig. 1c). The annual ~~cumumaled P (~~P_{cum}~~)~~ in the AD plot was lower by 273 mm than in the ND plot at the end of 2012 (782 compared to 509 mm). In 2013 the AD started only at the end of June, simulating a later amplification~~; our April and June 2013 measurements were thus not impacted by AD.~~. From August ~~to~~until October 2012, SW was 50~~ to ~~-90% lower in the AD plot than in the ND plot (≈ 0.02 and to 0.05 L_{H2O} L_{soil}^{-1} respectively in August, Fig. 1d). The AD plot soil water deficit remained significant until the end of the experiment (Mann~~ & ~~-Whitney, $P<0.05$ in June 2012, $P<0.001$ from July 2012 to June 2013), although the rain exclusion system was not activated between December 2012 and June 2013.

No significant difference was noticed for monthly PAR and *T* means between the ND and the AD plot, except in September 2012 when branches sampled on the ND plot received significantly more PAR than branches on the AD plot (Mann~~ & Whitney, P<0.001).~~-Whitney, $P<0.001$). This difference could be due to an orientation of the branches sampled in the ND plot in September that enabled greater receipt of PAR during our measurements than the AN sampled branches.

Formatted: Heading 2, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

3.2 ~~3.2 Physiology~~Gas exchange and isoprene seasonal variations

G_w and P_n showed similar seasonal patterns in both plots (Figs. 2a, 2b), with the lowest values in July-September (10-20 mol_{H2O} m^{-2} s^{-1} and ≈1 $µmol_{CO2}$ m^{-2} s^{-1} respectively~~)~~), and the highest in June (80-170 mol_{H2O} m^{2} s^{-1} and ≈9 $µmol_{CO2}$ m^{-2} s^{-1} respectively). Respiration dominated over gross CO_2 assimilation in April, resulting in negative net assimilation ($P_n \approx -1$ $µmol_{CO2}$ m^{-2} s^{-1}) in both plots. ~~By~~In contrast, G_w and P_n were not ~~similarly~~ influenced by water stress~~.~~ in the same way. Whereas G_w was significantly reduced under AD ~~since~~from July 2012, P_n remained stable, ~~expect~~except in June 2013 when ~~unexplained high~~ P_n values that were twice ~~higher~~as high under AD than ND were observed. ~~This higher value was~~

~~however attributed~~It is important to note that the tomography measurements made at this site showed that oak roots were predominantly distributed in the outermost humiferous horizon located above a calcareous slab at a 10-20 cm depth, and that only ~~one of the AD branches and was, moreover, unlikely to be due to AD since rain exclusion started in 2013 after June~~very few roots crossed this slab.

Water stress ~~impacted~~only affected the ER seasonal pattern during summer ~~alone~~ (Fig. 2c). Maximum ER was ~~one month~~ delayed by a month in the AD plot (104.8 µgC g_{DM}^{-1} h^{-1} in August) ~~compared~~in comparison to the ND plot (78.5 µgC g_{DM}^{-1} h^{-1} in July). ER was ~~the~~ lowest in October (≈ 6 µgC g_{DM}^{-1} h^{-1} in both plots). During April bud-break and isoprene emission onset, ER was as low as 0.5 and 1 µgC g_{DM}^{-1} h^{-1} in the ND and AD plot respectively.

Although ~~I_s~~$\varepsilon_{iso,Qp}$ was calculated every month as the slope of ER *vs* $C_L \times C_T$ (as in Guenther et al., ~~1993~~1995), this correlation was not significant in July, especially ~~for~~in the case of AD branches (P>0.05, R² = 0.06 and 0.01 for ND and AD respectively). As a result, ~~I_s~~ $\varepsilon_{iso,Qp}$ in July was ~~assessed in July~~calculated by averaging ER measured under environmental conditions close to 1000±100 µmol m^{-2} s^{-1} and 30±1~~-~~°C. In general, AD branches showed poorer ER *vs* $C_L \times C_T$ correlations than branches growing in the ND plot (data not shown).

~~I_s~~$\varepsilon_{iso,Qp}$ was significantly higher by a factor of 2 in August ~~(P=3.9)~~ and ~~in~~ September ~~(P=3.9)~~ for the AD branches compared to the ND (Fig. 2d). As for ER, ~~I_s~~$\varepsilon_{iso,Qp}$ maximum was reached in August (137.8 µgC g_{DM}^{-1} h^{-1}) in the AD plot, while the maximum in the ND plot occurred in July (74.3 µgC g_{DM}^{-1} h^{-1}). The general high variability observed in April during the isoprene emission onset ~~in April~~ (some branches were already emitting, while some were not yet emitting isoprene, regardless of their locations in the AD/ND plots) was as large as the AD-ND variability, and~~,~~ thus~~,~~ could not solely be attributed ~~only~~ to the water stress treatment. The relative annual ~~I_s~~$\varepsilon_{iso,Qp}$ difference between ND and AD ~~relatively to ND~~ was +45%.

3.3 ~~3.3~~ Modeling the isoprene seasonal variations of *Q. pubescens* at the O_3HP

~~Because we were aiming at testing an isoprene emission model widely employed for air quality applications, the empirical MEGAN model (Model of Emissions of Gases and Aerosols from Nature, Guenther *et al.*, 2006) was tested to assess our observed seasonal and drought variability of ER. A value of 53 µgC g_{DM}^{-1} h^{-1} was used for the emission factor I_s as given by Simpson *et al.* (1999) for *Q. pubescens*, together with a wilting point θw of 0.138 m^3~~

Formatted: Font: Not Italic

Formatted: Font: Not Italic

Formatted: Space After: 0 pt

Formatted: Heading 2, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

~~m^{-3} (Chen & Dudhia, 2001). Some agreement between the calculated and the measured ER in the ND plot was found in June 2012 & 2013, October and April measurements (Fig. 3a), although June 2013 ER were strongly (more than a factor of 5) underestimated by MEGAN. In contrast, under AD, ER was correctly assessed by MEGAN only in June 2012. During the driest months (July, August, September), under ND and AD, SW recorded at the O_3HP (0.05 m^3 m^{-3}, see Fig. 1d) being lower than the θw used in MEGAN (0.138 m^3 m^{-3}) calculated ER were set to zero. When SW effect was not selected in MEGAN, an overall understimation of 60 and 70% was still found in the ND and AD plots respectively, and no more than 50% of the seasonal variations were captured (data not shown).~~

Given that we were aiming to test the capacity of an empirically based isoprene emission model to describe seasonal ER variability and sensitivity to drought observed during this study, we tested the latest version of the MEGAN model, which is widely used for air quality and climate change applications (MEGAN2.1, Guenther et al., 2012). In particular, the ability of its soil moisture coefficient activity γ_{SM} (Eq. 4a-4c) to assess the observed effect of ND and AD treatments was examined over wilting point θ_w values ranging from 0.01 to 0.15 m^3 m^{-3}, representative of a large brand of soils (Ghanbarian-Alavijeh and Millàn, 2009). Indeed, Müller et al., (2008) showed that isoprene assessments were very sensitive to θ_w. For the record, θ_w was 0.15 m^3 m^{-3} at the O_3HP.

Assessed (ER_{MEGAN}) and observed (ER) isoprene emission rates were compared separately for ND and AD. However, given that the rainout shelter was implemented close to the commencement of our study in June 2012, measurements carried out in the AD plot were not distinguished, only in the case of this month, from the ones taken in the ND plot (AD and ND data were thus mixed for June 2012).

For θ_w<0.05 m^3 m^{-3}, and regardless of the θ_w value, MEGAN2.1 captured more than 80% of the ER variability in the ND plot ($y=0.15x^{1,5}$, R² =0.81, Fig. 3a), but less (≈ 50%) in the AD plot (R²=0.53 and 0.54 for θ_w=0.005 and 0.01 m^3 m^{-3} respectively, Fig 3b). An overall over-estimation of 25% was associated with the MEGAN2.1 assessment for both treatments. On the contrary, for $\theta_w \geq 0.05$ m^3 m^{-3}, most of the isoprene emissions were set to zero by MEGAN2.1 in the AD plot, while in the ND only June observations were correctly assessed with an overall over-estimation (whatever the θ_w values) of ≈ 10% (R² ranging from 0.76 to 0.80 for θ_w=0.15 and 0.1 m^3 m^{-3} respectively). If some of the July ER_{MEGAN} were fairly close to the observations for θ_w=0.1 m^3 m^{-3}, the overall correlation was poor (y=0.2x+49.5, R²=0,02).

Assuming that the discrepancies between ER_{MEGAN} and ER only resulted from the γ_{SM} formulation in MEGAN2.1 (and not from the other activity coefficients γ_P, γ_T or γ_A used, Eq. (3)), ER/ER_{MEGAN} was calculated for both ND and AD treatments and was considered against the measured SW. In the ND treatment, ER/ER_{MEGAN} was not found to be significantly dependent on SW ($y=0.653e^{10.52x}$, $R^2=0.13$, Fig. 4a). However, in the AD plot, ER/ER_{MEGAN} increased exponentially with SW ($y = 0.192e^{51.93x}$, $R^2=0.66$, Fig. 4b), and in particular when SW became higher than the wilting point θ_w measured at the O_3HP site (0.15 m^3 m^{-3}). Similar findings were obtained for SW-7, SW-14 and SW-21, for both the ND and AD treatments (Table 1).

In order to provide a better description of the impacts of ND and AD on ER as observed at the O_3HP, an empirical type model, based on ANN optimisation of our observations at the O_3HP, was developed specifically for *Q. pubescens* isoprene emissions. Training and validation of the different ANNs tested were made using values of ER, T, P, PAR, ST and SW measured at the O_3HP (COOPERATE database). Environmental regressors x_i were integrated, using daily means, over a period ranging from 0 to 21 days prior to the measurements.

Among the different ANN settings tested, ~~the *G*14~~an optimised architecture, *G*14 (lowest RMSE between calculated and measured values, no overtraining, best correlation between measured and calculated ER over the whole range of value, see Boissard et al., 2008) was found for N=3 and a set of 16 x_i with their corresponding connecting weights w_i (Appendix 1). The final optimised RMSE (validation data) was 8.5 µgC g_{DM}^{-1} h^{-1}, for ER values ranging from 0.06 to 113 µgC g_{DM}^{-1} h^{-1}, and represents 35% of the mean (22.7 µgC g_{DM}^{-1} h^{-1}). More than 80% of the ER seasonal variations were assessed by *G*14, whatever the water treatment (ND or AD) and the month, except in July (Fig. 5a) when ER variability was always poorly represented whatever the different ANN settings considered; an overall underestimation of 6% and 12% was observed in the ND and AD respectively. For comparison, ER_{MEGAN} calculated with a value θ_w of 0.15 m^3 m^{-3} are presented again in Fig. 5b for both the ND and AD treatment.

Formatted: Font: Not Italic

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

~~connecting weights w_i (Appendices 1). More than 80% of the ER seasonal variations were assessed by *G*14, whatever the water stress (ND or AD) and the month, except in July (Fig. 3b) when ER were always poorly represented whatever the different ANN settings considered.~~

~~Among the environmental regressors used in *G*14, SW was found – whatever the frequency considered – to be the dominant parameter to explain the observed ER seasonal variations,~~

~~especially when *Q. pubescens* was growing under AD (Fig. 4a). When water stress became significant in July, ER seasonal variations were found to be more sensitive to higher frequency changes in the environmental conditions (0 to 7 days before the measurement), whatever the regressors used, compared to April and June when ER were more sensitive to lower frequencies (14 to 21 days) for both ND and AD (Fig. 4b). On the overall, *T* and *L*, whatever their frequencies but in particular when considered instantaneously, did not account for more than 15% in the seasonal ER pattern.~~

~~**3.4 2100 projections**~~ Under ND, the global contribution of the two lowest frequencies (-14 and -21 days) considered in *G*14, was, relative to the contribution of the two highest frequencies (instantaneous and -7 days), higher than under AD (Fig. 6). In particular, in October 2012 and April and June 2013, the two lowest frequencies respectively represented 20, 97 and 50% of the total in the ND compared to 3%, 55% and 26% in the AD.

3.4 ER sensitivity to expected climatic changes over the European Mediterranean area

~~Relative changes between present and future climates were averaged on a monthly basis for the climate parameters used in *G*14 (SW, ST, *T*, PAR and *P*) and ER, according to the RCP2.6 and RCP8.5 scenarios (Fig. 5). PAR changes between present and future climates being negligible for both scenarios they are therefore not presented. Among the different *G*14 parameters, the highest monthly relative changes was found for *P* (+80% in March, RCP2.6) and ST (+105 and +120% in January and December respectively; RCP8.5, Fig. 5a).~~

~~The annual P_{cum} was found to be 1401 and 758 mm according to the RCP2.6 and RCP 8.5 projections respectively (data not shown), leading to an annual P_{cum} relative change of +6% and -24% for RCP2.6 and RCP8.5 respectively (Fig. 5a). Major *P* relative changes occur in late winter for RCP2.6 (a 50% increase) and during the summer for RCP8.5 (a strong decrease down to -90% in August). SW relative change profiles were found to be in line with *P*.~~

~~*T* relative changes were found to be always positive according to both scenarios, with an annual relative increase of 11% (+1.5 °C) and 41% (+5.4 °C) for the RCP2.6 and RCP 8.5 respectively (Fig. 5a). For both scenarios the strongest monthly changes were observed during the winter time (+50% and +87% in December for RCP2.6 and RCP 8.5 respectively), while the summer $\Delta T/T$ was of the order of +10 and +40% respectively. The ST relative change profiles were found to be in line with *T*.~~

Formatted: Heading 2, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

Formatted: Font color: Text 1, English (U.S.)

Formatted: Font: Not Bold, English (U.S.)

~~Monthly changes of ER calculated using *G*14 ($d\mathrm{ER}_{G14}$) generally increased under both scenarios, but more intensively under the extreme RCP8.5 (up to +52.8 and +13.8 µgC $\mathrm{g_{DM}}^{-1}$ h^{-1} in August for RCP2.6 and RCP8.5 respectively, Fig. 5b). The highest $d\mathrm{ER}_{G1}$ decreased was assessed in September for RCP2.6 (-2.4 µgC $\mathrm{g_{DM}}^{-1}$ h^{-1}, Fig. 5b). The corresponding monthly relative changes ($d\mathrm{ER}_{G14}/\mathrm{ER}_{G14}$) were maximal in July (+500%) and October (+800%) according to RCP2.6 and RCP8.5 respectively (Fig. 5c). On the overall, $d\mathrm{ER}_{G14}/\mathrm{ER}_{G14}$ was +70 and +320% for RCP2.6 and RCP8.5 respectively.~~

~~Whatever the projections, $d\mathrm{ER}_{G14}/\mathrm{ER}_{G14}$ was found to be relatively more impacted by water availability *W* (calculated as the sum of relative impact of SW and *P*) than by temperature effect (calculated as the sum of relative impact of ST and *T*): 67 and 63% for RCP2.6 and RCP8.5 respectively (Fig. 5d). By contract, temperature contribution became higher (more than 60%) in October and June under RCP2.6 and RCP8.5 respectively.~~

~~Whatever the *G*14 parameters used, the seasonal variations of $d\mathrm{ER}_{G14}/\mathrm{ER}_{G14}$ were mainly affected by 14-d frequencies (36.8 %, Fig. 5e), especially during early spring (65%) under the RCP2.6 scenario, while instantaneous variations of the *G*14 parameters became predominant (30.3 %) for the RCP8.5, and especially during summer (50 %). The lowest frequency (21-d) impact was similar for both scenarios and was close to 10% over the season~~

~~4.~~ Present and future *T*, *P* and PAR (ISI-MIP-derived), and SW and ST (ORCHIDEE-derived) were integrated over periods ranging from 0 to 21 days in order to be used in *G*14 and to assess ER_{G14} for present and future cases. Moderate (respectively, severe) changes with regard to the present of SW, *P*, ST, *T* and PAR were additionally calculated according to RCP2.6 (respectively, RCP8.5) scenario; however, PAR relative changes were not considered as they were negligible for both moderate and severe scenarios.

Moderate changes of the environmental conditions (RCP2.6 scenario) implied a systematic positive monthly ΔT throughout the year, whereas ΔP was found to be positive only during the winter and negative during the summer (Fig. 7a). ST and SW changes were found to be in line with *T* and *P* respectively. The highest monthly relative changes were for *P* (+75% in February and -30% in July), whereas the smallest were for SW. Monthly ST and *T* relative changes remained more or less constant (between +7% and +10%) between February and November. Overall, *T* and P_{cum} absolute (relative) annual changes were +1.4°C and +34 mm respectively (+9.1% and +4.8% respectively, Table 2).

Under more severe environmental changes (RCP8.5 scenario), monthly *T* and ST increased all year round, whereas *P* and SW generally decreased, except in January, February and November, when relative *P* changes were negligible (Fig. 7b). The annual absolute (relative) changes for *T* and P_{cum} were +5.3°C and -124 mm respectively (+34% and -24%, respectively, Table 2). In these conditions, the annual $\Delta P_{cum}/P_{cum}$ was similar to the reduction experienced at the O$_3$HP during our study (-30%). The highest monthly relative changes were found for ST: +96% and +86% in January and December respectively. During summertime the highest relative changes were found for *P* (-55% and -62% in July and August respectively).

ER$_{G14}$ was found to systematically increase compared to the present under 'T' and 'TT' changes, with an annual relative change of +80% and +240% respectively (Fig. 8a). The highest relative changes were noted in June and July. In contrast, ER$_{G14}$ was almost not sensitive to 'P' or 'PP' changes, whatever the month (annual relative change of +10% and +8% respectively, Fig. 8b). When the combined impacts of changes in temperature and precipitation were considered, ER$_{G14}$ was found to systemically increase all year round, following a seasonal trend that was extremely close to that found for the 'T' and 'TT' tests (Fig. 8c). However, the additional effect of the precipitation changes enhanced the increase noticed for temperature changes only: the annual increase was +100% ('T+P') and +280% ('TT+PP') compared to +80% ('T') and +240% ('TT'). Note that the ER$_{G14}$ seasonal trend calculated for the present did not match our observed ER variations. Indeed ER$_{G14}$ was tuned using environmental parameters averaged over 24 hours (and therefore integrated over the daytime and night-time period), and were thus much lower than the environmental parameters measured during our daytime-only samplings (especially for PAR and *T*).

4 Discussion

4.1 ~~4.1 Water~~**Impact of water stress ~~impacts~~ on ~~the~~ seasonal gas ~~exchange~~exchanges and isoprene emission of *Q. pubescens***

~~Despite~~In spite of a significant G_w reduction in summer 2012 ~~due~~owing to the AD, *Q. pubescens* maintained a positive P_n during ~~all~~the summer, regardless of ~~the~~ water stress (ND or AD). Electric resistivity tomography measurements carried out on the O$_3$HP site revealed the heterogeneity of the karstic substrate, organised as soil pockets developed between limestone rocks. Water and nutrient pools and dynamics probably differed greatly between the shallow upper soil layers and the soil pockets developed between limestone rocks. However, the soil trenches in the site revealed that a calcareous slab often developed at a depth of 10-20 cm and that the roots of the oaks were often distributed in this humiferous

Formatted: Line spacing: single

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: Heading 2, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

Formatted: English (U.S.)

Formatted: Font: Italic, English (U.S.)

Formatted: Font: Not Bold, English (U.S.)

horizon close to the surface, with very few roots crossing this slab. Water supply from layers deeper than 10-20 cm was thus not considered. Such behaviour enables trees to limit ~~the~~ evapotranspiration under water stress, and~~,~~ as a drought-acclimated species~~,~~ permits them to ensure ~~enough~~ sufficient accumulation of carbohydrates ~~accumulation~~ for the winter (Chaves et al., 2002). Such strategy was also observed in a study conducted on the same species but under greenhouse conditions ~~(Genard-Zielinski *et al.*, 2014).~~(Genard-Zielinski et al., 2015). The seasonal regulation/conservation of P_n and G_w enabled isoprene emissions to be maintained even during the summer water stress (ND and AD).

The maximum $\varepsilon_{iso,Qp}$ in both plots was close to previously measured values obtained for the same species under Mediterranean conditions during greenhouse and *in-situ* experiments (114.3 and 134.7 µgC.g$_{DM}^{-1}$.h^{-1}) by Genard-Zielinski et al. (2015) and Simon et al. (2005) respectively. The difference observed in April 2013 between $\varepsilon_{iso,Qp}$ in the ND and AD could not be attributed solely to the AD effect. Indeed, apart from a possible 'memory effect' of the AD applied during 2012, the observed difference was probably due to the high natural variability in bud-breaking and isoprene emission onset at this point of the year. The observed significant increase (a factor of 2) of ~~the tree capacity to emit isoprene~~$\varepsilon_{iso,Qp}$ under AD (August and September) illustrates how isoprene is likely to be important for short-term *Q. pubescens* drought-resistance, in particular through the ability of isoprene to stabilise the thylakoids membrane, under~~,~~ (for example~~, a~~) thermal or oxidative stress ~~as shown for *Populous* species (~~(Peñuelas et al. 2005; Velikova et al~~.,~~. 2012). ~~Previous~~Moreover, previous studies have highlighted the possibility for a plant growing under ~~a~~ water stress to synthesise isoprene using an alternative carbon source (extra-chloroplastic carbohydrates~~,~~) (Lichtenthaler et al., 1997; Funk et al., 2004~~). Interestingly, the maximum I_s value was very similar for both treatments (≈ 140 µg.g$_{DM}^{-1}$.h^{-1}) but was reached one month later under the AD (August compared to July). These observations strengthen the hypothesis that, under environmental stresses (like water stress), some plants favour the allocation of carbon to secondary metabolites production (such as isoprene) rather than allocation to growth. Maximum I_s was very close to previously measured values obtained for the same species under Mediterranean conditions during greenhouse and *in situ* experiment (114.3 and 134.7 µg.g$_{DM}^{-1}$.h^{-1}, Genard-Zielinski *et al.*, 2014; Simon *et al.*, 2005 respectively). The difference observed in April 2013 between I_s in the ND and AD plot cannot be attributed only to the AD effect, since the rain exclusion was started only at the end of June 2013; apart from a possible 'memory effect', it is likely due to the high natural variability in bud breaking and isoprene emission onset at this period of the year~~; Brili et al., 2007). For species emitting other BVOC than isoprene, but studied in the Mediterranean area under water stress, Lavoir et al. (2009) reported lower (a factor of ≈2) monoterpene emission rates from *Quercus ilex* under AD from June to August, during the 2nd and 3rd year of rain exclusion. Since *Q. ilex* does not possess specific

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Not Italic

Formatted: Comment Text, Tab stops: Not at 8 cm

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt, Italic

Formatted: Font: 12 pt

leaf reservoirs for monoterpene storage, *Q. ilex* monoterpene emissions are hence *de novo* and their emissions are tightly related to their synthesis according to light and temperature as isoprene.

The ~~strong~~significant uncoupling between ER and $C_L \times C_T$ reported for the July measurements occurred when ~~soil water content conditions~~SW significantly decreased ~~at the O_3HP, in both plots, down~~ to their seasonal minimum values (0.05 and 0.03 m^3 m^{-3}~~). Such an~~) at the O_3HP in both plots. A similar uncoupling ~~was~~has also been observed for some other strong isoprene emitters under water stress (*Quercus serrata* ~~Murray and Blume~~, *Quercus crispula*, Tani et al., 2011). ~~It confirms the assumption of~~These findings may confirm these ~~authors~~authors' assumptions that extra-chloroplastic isoprene precursors supply the carbon basis for isoprene biosynthesis (and not only from CO_2 fixed instantaneous in the chloroplast) when water stress occurs, ~~explaining~~which explains why isoprene emissions become less dependent ~~of~~on the classical abiotic factors PAR and *T* as considered ~~in the empirical MEGAN model, or the other environmental abiotic regressors tested in this study. However, our statistical approach used in this study would require a larger set of data to further investigate this particular point.~~ by Guenther et al. (1995).

4.2 ~~4.2 Towards what~~ Improving consideration of the drought effect in isoprene emission ~~modeling improvement?~~models

~~Since most of the empirical isoprene emission algorithms of MEGAN have been developed from measurements carried out under 'optimal' (*i.e.* 'none stressing') conditions, they still show difficulties in capturing the impacts of various stress conditions, such as the water deficit, for instance. Hence, ER measured during this study, was observed to be rarely dependent on *T* and PAR only: indeed, except in June (e.g. just before the ND and AD onset), MEGAN was unable to predict isoprene emission variations. In particular in July, the strong uncoupling between ER and $C_L \times C_T$ illustrates the extent to which other additional parameters than the abiotic parameters *T* and PAR should be taken into account in isoprene MEGAN algorithm in order to better capture the shift from carbon allocation to growth towards secondary metabolites synthesis during reduced water availability conditions.~~

~~Our approach in developing a specific algorithm for *Q. pubescens* (*G*14) confirmed the strong~~Since ND and AD conditions tested by *Q. pubescens* in our study stood aside from optimal growth conditions under which empirical emission models perform fairly well, it was interesting to test the ability of MEGAN2.1 to reproduce the observed impacts of a water deficit, as in O_3HP, on isoprene emissions. The formulation of the MEGAN2.1 soil moisture

Formatted: Font: 12 pt, English (U.S.)

Formatted: Comment Reference, Font: 12 pt, Font color: Auto, English (U.S.)

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt, Italic

Formatted: Font: 12 pt

Formatted: Font: 12 pt, Italic

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font: 12 pt

Formatted: Font color: Auto

Formatted: Heading 2, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

Formatted: English (U.S.)

Formatted: Font: Not Bold, English (U.S.)

factor γ_{SM}, wilting point-centred, was deemed inadequate to reproducing the observed isoprene variability of a drought-adapted emitter such as *Q. pubescens*. Thus, MEGAN2.1 very successfully reproduced observed ER variability under the ND (more than 80%) only when γ_{SM} was not operating; in fact, only when very low values of the wilting point were selected ($\theta_w \leq 0.01$ m^3 m^{-3}), γ_{SM} was set to 1. In practice, wilting point values lower than 0.01 m^3 m^{-3} are encountered very rarely, and only for loamy sand soils (Ghanbarian-Alavijeh and Millàn, 2009), and so did not apply in the case of *Q. pubescens* in the present study. Once higher θ_w (≥ 0.05 m^3 m^{-3}) were tested, γ_{SM}, and with it almost all the isoprene emissions, rapidly decreased to zero once the drought was underway (i.e., after the June measurements). On a larger scale (over the subtropical Africa), Müller et al. (2008) found that MEGAN underestimation of isoprene emissions were also the largest after the drought was reached. Consequently, for a drought-adapted isoprene emitter, not only was the wilting point not found to be a relevant parameter to be considered in the expression of γ_{SM}, but also a formulation that could stop isoprene emissions, whatever the drought intensity.

The fact that under ND the discrepancies between ER$_{MEGAN}$ and ER were not found to be contingent on the soil water content SW (Fig. 4a) illustrates that under a natural drought intensity, the capacity of a drought-resistant species to emit isoprene, that is to trigger physiological regulations to protect its cellular structures, is primarily due to its natural adaptation, and not to the water available in the soil. Isoprene emissions became SW dependent only when the adaptation of *Q. pubescens* to its 'natural' environment was threatened (i.e., the AD treatment, Fig 4b). Thus, for a species that is not adapted to drought, such as *Populus deltoides*, the appearance of unusual water stress conditions would strongly affect and limit its isoprene emissions, as previously reported by Pegoraro et al. (2004). Indeed, this reference is the only one used by Guenther et al. (2006) to account for the impact of the soil water content in ~~the Mediterranean area, and not only under stress conditions. However, the SW effect as considered in the MEGAN isoprene model was found to be not adapted to account for *Q. pubescens* capacity to resist to water stress: isoprene emissions did not decrease nor cease under ND or AD conditions as expected in summer by MEGAN; on the contrary, they were observed to be maintained, and even increased, during the maximum AD period when SW became lower than the wilting point θw. Since the SW availability modulation (1 to 0) used in MEGAN was based on the single observation made by Pegoraro *et al.* (2004) between *Populus deltoids* photosynthesis and stomatal conductance to water vapour, it is obviously not appropriate for water stress-resistant species.~~MEGAN2.1; the γ_{SM}

Formatted: Font color: Text 1, English (U.K.)

factor cannot effectively account for isoprene emission variability for drought-adapted emitters such as *Q. pubescens*. Such a discrepancy under conditions other than Mediterranean was also noticed by Potosnak et al~~., ~~. (2014) during a seasonal study over a mixed broad-leaf forest ~~mainly~~primarily composed of *Q. alba* L. and *Q. velutina* Lam. (Missouri, USA). ~~Although they found that MEGAN robustly captured 90% of the observed variance during most of the annual cycle, it was unable to reproduce the time-dependent response of isoprene emission to water stress (θw of 0.084 m^3 m^{-3}). Improved isoprene empirical models should be able to more realistically account for the drought adaptation by the emitter. One way could be, for MEGAN, to add an emitter-dependent parameter in the general isoprene algorithm. Moreover,~~ Guenther et al. (2013) have suggested that including the soil moisture, averaged over longer ~~time~~ periods of time (such as the previous month and not only the mean over the previous ~~240h~~240 hours) may help to ~~yield better~~improve predictions during drought periods. ~~Note~~In this study we found that ~~MEGAN performed better on our experimental data when its SW modulation was set to 1 (no SW effect), since almost half of the isoprene variations were then assessed, whatever~~ the ~~water stress intensity; however a general underestimation of a factor of 2 remained (data~~ discrepancies between ER_{MEGAN} and ER were not ~~shown).~~

~~Our work also highlighted~~ related to the ~~seasonal change occurring in the regulation~~ frequency ~~of isoprene emissions, especially when stressed environmental conditions appeared. Indeed, *Q. pubescens* isoprene emissions became more highly sensitive to rapid environmental changes as drought intensity increased: in June 2012, ER_{G14} variations were mainly controlled by a 14-day frequency (under ND and AD) while they became later in the season mainly 7-day, and even 0- to 7-day dependent as soon as the ND and AD, respectively, increased (Fig. 4). Moreover, only a small fraction of ER_{G14} variations were due to instantaneous environmental variations changes (as mostly accounted for in MEGAN). The highlighting of a dynamical regulation~~ over ~~oak seasonal leaf development and of a lower than instantaneous frequency dependency of their isoprene emission was also made for *Q.*~~ which SW was considered (Table 1): under ND they remained SW independent, whereas under AD the correlation between ER/ER_{MEGAN} and SW remained of the same order ($0.66 \leq R^2 \leq 0.38$), but with a best fit found for the soil water content of the current day. These findings suggest that the formulation of the soil moisture activity factor could be improved in MEGAN2.1 if at least two distinct types of isoprene emitters were considered: (i) non-drought-adapted species (such as *Populus deltoides*) from which isoprene emissions would be modulated using the actual γ_{SM} formulation; (ii) drought-adapted emitters (such as *Q.*

Formatted: Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1

Formatted: Font: Not Italic

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Not Italic

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: English (U.S.)

Formatted: English (U.S.)

Formatted: Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1, English (U.K.)

pubescens), for which γ_{SM} would modulate isoprene emissions relative to SW, without diminishing them to zero, in an exponential way similar to the expression found in this study: $\gamma_{SM} = 0.192e^{51.93\ SW}$ (see Section 3.3). However, validation of such an expression to other drought-adapted isoprene emitters, as well as to other drought-adapted BVOC emitters, is required and will necessitate further field/controlled *ad hoc* experiments.

Moreover, the largest discrepancies between ER_{MEGAN} and ER were noticed for the measurements in April and for some of those in June (Figs. 3 and 4), i.e., in periods when the drought (whether natural or amplified) was yet to be completely underway during our study. This highlights that ER variability during the onset and seasonal increase of isoprene emissions was not solely drought- or SW-dependent, even in a water-limited environment such as the O$_3$HP. Indeed, as observed for *Q. alba* and *Q.* ~~*alba* and *Q.*~~ *macrocarpa* ~~(Geron *et al.*, 2000; Petron *et al.*, 2001 respectively):~~Michx, the isoprene onset was ~~observed~~found to ~~also~~be strongly ~~correlate~~correlated with ambient temperature cumulated over ≈2 weeks (200 to 300 degree day, ~~d.d.,~~Dd, °C~~)~~), while the maximum ER was observed at 600-700 ~~d.d.~~Dd °C~~.~~ ~~If~~ (respectively Geron et al., 2000 and Petron et al., 2001). However, if part of this dynamical regulation is already included in ~~the leaf age~~MEGAN2.1 through its emission activity factors γ_T and γ_{A}~~$_{,i}$~~ (see Eq. 3), the combined effect of ~~MEGAN isoprene emission algorithm, the part due to the impacts of stressing conditions is not yet considered, and~~ temperature regulation and drought is not ~~only when the plant is experiencing a drought period.~~fully accounted. For instance, Wiberley et al. (2005) observed that the onset of kudzu isoprene emissions ~~were~~was shortened by one week under elevated temperature compared to cold growth.

~~On one side, and as suggested by Zheng *et al.* (2015), ad-hoc long-term direct measurements~~ ER_{G14} consequently became more sensitive to rapid environmental changes as drought intensity increased: the overall averaged relative contributions of the regressors x_i cumulated over 14 and 21 days decreased by 45% and 29% in the ND and AD respectively. Interestingly, these changes were found to be highest during the months of October 2012 (35% and 8% in the ND and AD respectively), April 2013 (from 96% to 55% in the ND and AD respectively) and June 2013 (49% and 26% in the ND and AD respectively, Fig. 6). Therefore, during the senescence and onset periods, the drought affected the dynamical regulation of isoprene emission ~~as the one performed at the O$_3$HP, are still essential to provide further information for empirical model improvement on how isoprene emissions are seasonally affected by water availability. However, on the other side, representation of soil moisture in land-surface and climate models is currently poor (Köstner *et al.*, 2008).~~

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Not Italic, Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1, English (U.K.)

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Italic

Formatted: Font color: Text 1

~~Consequently, further actions need to be undertaken in order to provide a better description of soil moisture at the surface (*e.g.* the NASA Soil Moisture Active Passive instrument) and thus improve the representation of the effective water available for plants in emission models.~~more than the emissions themselves. Thus, an ANN approach as used in this study to develop *G*14 highlights the importance of including a modulation along the season of the range of frequencies over which the relevant environment regressors should be considered.

4.3 ~~4.3 What~~How will climatic changes affect the seasonal variations of *Q. pubescens* isoprene emissions in the Mediterranean area?

In the future ~~**impacts of amplified drought on isoprene emissions?**~~

~~Depending on the future scenario tested, changes in precipitation (thus in soil water content) and/or in temperature will differently affect~~ , the Mediterranean area ~~tested in our study.~~ ~~A net P_{cum}~~ investigated in this study will face changes in terms of precipitation regime (thus of soil water content), and/or changes in ambient temperature (thus of soil temperature). Depending on the CO_2 trajectory scenario considered, the annual P_{cum} would remain more or less stable (RCP2.6), or decrease by 24% (RCP8.5); however, the seasonal regime would change, with a summer reduction ~~was predicted only under the extreme CO_2 trajectories RCP8.5, with an annual decrease of 24%, similar to the AD applied at the O_3HP site during our study (-30% of precipitation), together with strong temperature increase (+5.4 °C). On the contrary, the only main change predicted under the RCP2.6 scenario was a moderate temperature increase (+1.5 °C), whereas the annual predicted P_{cum} remained more or less stable (a slight +6% increase, due to heavier rain falls in winter). In terms of AD, the~~of *P* in both cases. The O_3HP experimental strategy ~~followed during~~used in this work ~~illustrated~~illustrates the upper limit of the drought intensity that *Q. pubescens* ~~should~~could undergo ~~on the~~by 2100 ~~horizon~~ in the Mediterranean area. On the other hand, temperature would increase regardless of the scenario and month, from 1.4 (+10%) to 5.3°C (+34%) annually.

~~The mere RCP2.6 *T* increase had a similar predicted impact on ER$_{G14}$ relative change (+70%) than the mere precipitation reduction had on our observed ER (+45%). If an isoprene emission increase is generally predicted and observed in relation with future temperature enhancement (Peñuelas & Staudt, 2010), such a response seems not so clear under Mediterranean water deficit conditions (Llusià *et al.*, 2008, 2009). In our case, when the~~

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

~~combined effects of temperature and drought increase were considered (RCP8.5 scenario), the predicted ER$_{G14}$ relative changes were enhanced compared to the sum of the individual relative effects of drought and temperature: on the average, ER$_{G14}$ was multiplied by a factor of 3 (RCP8.5, Fig. 5c). During summer, this enhancement was particularly pronounced when the drought became maximum (August) with ER$_{G14}$ relative changes nearly 10 times higher under the RCP8.5 than the RCP2.6 (+430 and +46% respectively). Yet, the highest predicted enhancement occurred when the drought period ended, in October, with ER$_{G14}$ increased by a factor of 8 under RCP8.5. In addition to expected high *d*ER$_{G14}$/ER$_{G14}$ values during the drought period, the main relative change in isoprene emission would actually occur in autumn. This prediction is in agreement with observations made on different emitters in the Mediterranean area where isoprene emissions were observed in autumn to reach levels as high as in spring as soon as the water stress is declining and the net assimilation, hence the isoprene emissions, are favored again (*e.g.* Owen *et al.*, 1998). Moreover, the relative effect of *T* on *d*ER$_{G14}$ was predicted to increase and became even higher (up to 64%, RCP2.6) or similar (RCP8.5, Fig. 5d) to the *W* relative effect in October, as soon as drought intensity lowered: ER and *T* variations became, again, highly coupled as in the current isoprene algorithms (*e.g.* G95, Guenther *et al.*, 1995). However, in June, the relative higher *T* effect on *d*ER$_{G14}$ compared to *W* (60 *vs* 40%, RCP8.5, Fig. 5d) could illustrate a higher sensitivity of *Q. pubescens* isoprene emissions to temperature stress as the drought is setting in. Such a co-effect was also observed by Genard-Zielinski (2014) on *Q. pubescens* branches that were growing in the AD plot. Except in June and October, *d*ER$_{G14}$/ER$_{G14}$ seasonal variations were predicted to become mainly driven by the water budget (more than 65%) compared to temperature (less than 35%), whatever the scenario used.~~

~~These 2100 projections were made~~As expected, ER$_{G14}$ was found to increase appreciably with temperature increase, from 80% annually in the RCP2.6 scenario to 240% in RCP8.5 (Fig. 8a). If such an increase is generally estimated and observed when considering a range of temperature enhancements that accord with future projected changes (Peñuelas and Staudt, 2010), such a response seems fairly unclear under Mediterranean water deficit conditions (Llusià et al., 2008, 2009). On a global scale, Müller et al. (2008) estimated a 20% decrease of isoprene due to soil water stress. In our case, isoprene emissions were found to be scarcely sensitive to *P*, whatever the intensity of changes: at most, annual *P* would increase isoprene emissions by 10%, regardless of the intensity of *P* changes investigated over the scenario considered (Fig. 8b). This finding is in line with our observations: except in October 2012, monthly averaged ER were not significantly different in the ND and the AD (Fig.2c).

However, if the observed SW did differ between the ND and the AD plots (≈ a factor of 2, Fig. 1), SW calculated by the ORCHIDEE model was almost entirely unaffected by the *P* changes, even in the severe scenario RCP8.5. Such an uncoupling between *P* and SW could be explained by modifications in the ORCHIDEE model of the overall soil water evapotranspiration, runoff and drainage which in short lead to near-constant SW values. In order to test the impact of the sole SW changes within a similar range to that observed at the O_3HP between ND and AD, ER_{G14} seasonal variation was calculated using present SW multiplied every day by 0.5, 0.75, 1.5 and 2 (Fig. 9). Surprisingly, ER_{G14} was almost unchanged when SW was reduced (-2% and -13% annually for 0.5×SW and 0.75×SW respectively). ER_{G14} increased only when SW increased: +51% and +93% annually for 1.5×SW and 2×SW respectively. These results are in line with our findings that, under a certain level of SW, isoprene emissions from a drought-adapted emitter such as *Q. pubescens* are no more affected by soil water content. Indeed, under ND, ER/ER_{MEGAN} was not correlated with SW, but under AD, ER/ER_{MEGAN} remained more or less stable when SW was lower than the wilting point (Fig. 4 and Section 3.3). Isoprene emission variations would be highly SW-dependent only for the highest SW values: (i) in the spring and in the beginning of the summer when the drought is not completely underway; (ii) in the fall when the drought stress is fading away and when the highest differences are assessed between ER_{G14} calculated for SW-present and for 2×SW (Fig. 9). When the *T* and *P* effects were combined, the seasonal variation of ER_{G14} was affected in a similar way to when the sole *T* effect was considered, but with an enhanced increase: +20% and +40% between 'T' and 'T+P' tests, and between the 'T+P' and 'TT+PP' tests respectively (Figs. 8a and 8c). Such higher sensitivity of *Q. pubescens* isoprene emissions to temperature stress under drought was also observed by Genard-Zielinski (2014). Understandably, the *G*14 algorithm developed in this study to assess isoprene emissions in future climates should be validated through a longer period of measurement, in order to assess how *Q. pubescens* acclimates over a more extensive period of drought, and to confirm or deny these findings. In this context, measurements have been carried on at the O_3HP on the same branches as the ones studied in this work since June 2013 (Saunier et al., 2017).

These findings were attained considering an unchanged *Q. pubescens* biomass, i.e~~. not affected~~., unaffected by long~~-~~-term acclimation to *T* and drought increase. However, one can question~~, on the one hand, if~~ whether *Q. pubescens* could maintain such a high allocation of its primary assimilated carbon (primary plant metabolites, PPMs) to isoprene emissions (secondary plant metabolites, PSMs). ~~Indeed, for a constant assimilation, the PSMs/PPMs~~

Formatted: Font color: Text 1

Formatted: Font: Not Italic, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

~~ratio could, on the overall, be multiplied by up to a factor of 3, and could reach a 7 fold increase during the highest drought periods (Saunier *et al.*, under review). Genard-Zielinski *et al.* (2014) showed that, under moderate and severe drought, *Q. pubescens*~~ Indeed, Genard-Zielinski et al. (2015) have shown that under moderate and severe drought, *Q. pubescens'* aerial and foliar growth ~~was~~is negatively affected. ~~Furthermore, on a~~Thus, in the long term, such a cost of drought could ~~impact~~affect the overall energy budget and ~~speed up the~~expedite plant senescence (Loreto ~~&~~and Schnitzler, 2010). ~~Our predicted isoprene emission increases~~ The assessed ER_{G14} increase could then be offset~~,~~ or even reversed.

On the other hand, one should also consider the additional co-effects of the CO_2 increase expected ~~a year by 2100.~~in the future. Bytnerowicz et al. (2007) have reported that~~,~~ if ~~the~~ temperature increase ~~would~~proves to have little effect, ~~an~~ elevated CO_2 would ~~favor~~favour both the growth and water use efficiency of plants, and account for a 15-20% increase ~~on~~in forest NPP. When CO_2 enhancement was considered, the leaf mass ~~(g)~~ per square ~~meter~~metre of the PFT ~~ground (broad leaf temperate)~~ tested in ORCHIDEE ~~during~~in this ~~work~~ study (broad-leaf temperate) was predicted to~~, relatively,~~ undergo a relative increase by 35% and 100 % under RCP2.6 and RCP8.5 respectively. Tognetti et al. (1998) observed a similar positive effect on the assimilation rate of both *Q. pubescens* and *Q. ilex* during a long~~-~~-term CO_2 enhancement study, and measured a net increase in the diurnal course of isoprene emissions. Thus, the major impact of future climate change on isoprene emissions could eventually be related to a general change in land cover, with Mediterranean species shifting to more favourable conditions.

~~Understandably, the *G14* algorithm should be validated on a longer period of measurements in order to assess how *Q. pubescens* acclimate over a longer period of drought, and confirm or deny these projections. In that context, since June 2013, measurements have been continued at the O_3HP on the same branches as the ones studied in this study (Saunier *et al.*, under review). However, the major impact of the future climate changes (higher drought, temperature and CO_2) on isoprene emissions could, eventually, be related to the expected general land cover change, with a shift of the actual Mediterranean species to more favorable conditions. Such impacts can only be assessed with - improved - isoprene emission models coupled with global dynamic vegetation models.~~

5 Conclusion

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Pattern: Clear (White), Tab stops: 6.25 cm, Left + 15.75 cm, Right + 19.39 cm, Left + 21 cm, Left + 22.62 cm, Left + 24.23 cm, Left + 25.85 cm, Left

Formatted: Font: Not Italic

Formatted: Font: Italic

The study carried out in 2012-2013 at the O_3HP on *Q. pubescens* was the first to test *in natura* and on a seasonal scale the effects of drought (ND and AD) on gas exchange, and in particular isoprene emissions of a mature coppice. This unique set of experimental data has confirmed how a drought-adapted species was able (i) to limit its evapotranspiration under water stress, even in summer, in order to maintain a similar level of net assimilation whatever the drought intensity and (ii) to emit similar or even higher amounts of isoprene in order to protect cellular structures under drought (ND or AD) episodes. In an environment such as the O_3HP (elevated ambient temperature and scarcity of the water available), and for a drought-adapted emitter such as *Q. pubescens*, isoprene emissions were thus maintained, and in the ND, their variability was not dependent on the soil water content. However, under the AD treatment, isoprene emissions were found to exponentially decrease with SW, in particular when SW was lower than the wilting point measured at the site (θw = 0.15 m^3 m^{-3}).

Since the intensity of isoprene emissions in the Mediterranean area is large, and can occur together and close to large urban emissions of other reactive compounds (in particular NOx emissions), the impacts of future environmental changes on isoprene emissions in this area need to be assessed as precisely as possible. The latest version of the empirical isoprene model, MEGAN2.1 was found to be unable to reproduce the effect of drought on isoprene emissions from *Q. pubescens*, regardless of the drought intensity (ND or AD). However, for such a drought-adapted emitter, MEGAN2.1 performed very well to capture the seasonal ER variability (more than 80%) under ND when its soil moisture activity factor γ_{SM} was not operating (γ_{SM}=1); this performance decreased to ≈50% in the AD treatment. We suggest that, in addition to the actual γ_{SM} expression, which is only valid for non-drought-adapted emitters, a specific formulation should be considered for drought-adapted emitters involving an exponential decrease of isoprene emission with SW decreasing to above-zero values, as proposed in this study for *Q. pubescens*. An ANN approach similar to that undertaken to develop *G*14 highlighted its ability to extract from appropriate field data measurements the relevant environmental regressors to be considered and the relevant frequency over which they should be employed. *G*14 was able to reproduce more than 80% of the ER seasonal variability observed for *Q. pubescens*, whatever the drought intensity. Moreover the application of *G*14 to future climate environmental data derived from IPCC RCP2.6 and RCP8.5 scenarios suggests that isoprene emissions in the future will be mainly affected by warmer conditions (up to an annual 240% increase for the most severe warming scenario), not by drier conditions (at most, a 10% increase annually). The major impact of amplified drought will actually consist of enhancing (by up to 40%) the sensitivity of isoprene emissions to thermal stress.

Acknowledgements. We are particularly grateful to P. E. Blanc, J. C. Brunel G. Castagnoli, A. Rotereau and other OHP staff for support before and during the different campaigns. We thank members of the DFME team from IMBE: S. Greff, C. Lecareux, S. Dupouyet and A. Bousquet-Melou for their help during measurements and analysis. This work was supported by the French National Agency for Research (ANR) through ~~project~~the projects CANOPÉE (ANR-2010 JCJC 603 01) and~~ project~~ SecPriMe^2 (ANR-12-BSV7-0016-01), INSU (ChARMEx), CNRS National program EC2CO-BIOEFECT (ICRAM project), CEA, and Université Paris Diderot-Paris 7. We are grateful to ADEME/PACA for PhD funding. For O$_3$HP facilities, the authors thank the research federation ECCOREV FR3098 and the LABEX OT-Med (no. ANR-11-LABEX-0061~~)~~), funded by the French Government through the A*MIDEX project (no. ANR-11-IDEX-0001-02). The authors thank the MASSALYA instrumental platform (Aix Marseille Université, lce.univ-amu.fr) for the analysis and measurements used in this publication

References

Affek, H. P. and Yakir, D.: Natural abundance carbon isotope composition of isoprene reflects incomplete coupling between isoprene synthesis and photosynthetic carbon flow, Plant Physiol., 131, 1727–1736, 2003.

Ashworth, K., Boissard, C., Folberth, G., Lathière, J., and Schurgers, G.: Global modelling of volatile organic compound emissions, in: Biology, Controls and Models of Tree Volatile Organic Compound Emissions, –Tree Physiology 5, edited by Niinemets, Ü., Monson, R.K., Springer Science + Business Media, Dortrecht, The Netherlands, 451–487, 2013

Atkinson, R. and Arey, J.: ~~Atmospheric~~Gas phase tropospheric chemistry of biogenic volatile organic compounds~~. Accounts Chem. Res., 31, 574–583, 1998~~: a review, Atmos. Env., 37, 197–219, 2003.

Blanch, J. S., Peñuelas, J., Sardans, J., and Llusià, J.: Drought, warming and soil fertilization effects on leaf volatile terpene concentrations in Pinus halepensis and Quercus ilex, Acta Physiol. Plant, 31, 207–218, 2009.

Boissard, C., Cao, X. L., Juan C. Y., Hewitt, C. N., and Gallagher, M.: Seasonal variations in VOC emission rates from gorse (Ulex europaeus), ~~-~~Atmos. Environ., 35, 917–927, 2001.

Formatted: Heading 1 Char, Font: Not Italic, French (France)

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Strong, Font color: Auto, English (U.K.)

Formatted: Font: Not Bold

Formatted: Font: Not Bold, English (U.S.)

Formatted: Font: Times, Font color: Black, English (U.K.)

Formatted: Level 1, Line spacing: single

Boissard, C., Chervier, F., and Dutot, A. L.: Assessment of high (diurnal) to low (seasonal) frequency variations of isoprene emission rates using a neural network approach, ACP., 8, 2089–2101, 2008.

Brili, F., Barta, C., Fortunati, A., Lerdau, M., Loreto, F., and Centritto M.: Response of isoprene emission and carbon metabolism to drought in white poplar (*Populus alba*) saplings, New Phytol., 175(2), 244-254, 2007.

Brüggemann, N. and Schnitzler, J.: Comparison of isoprene emission, intercellular isoprene concentration and photosynthetic performance in water-limited oak (Quercus pubescens Willd. and Quercus robur L.) saplings, Plant Biol., 4, 456–463, 2002.

Bytnerowicz, A., Omasa, K., and Paoletti, E.: Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective, Environ. Pollut., 147, 438–445, 2007.

Calfapietra, C., Fares, S., and Loreto, F.: Volatile organic compounds from Italian vegetation and their interaction with ozone, Environ. Pollut., 157, 1478–1486, 2009.

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukouli, C., Aprea, E., Maerk, T. D., Gasperi, F., and Biasioli F.: On quantitative determination of volatile organic compound concentrations using Proton Transfer Reaction Time-of-Flight Mass Spectrometry, Environ. Sci. Technol., 46, 2283–2290, 2012.

Chameides, W. ~~-~~L., Lindsay, R. W., Richardson, J., and Kiang, C. S.: The role of biogenic hydrocarbons in urban photochemical smog - Atlanta as a case-study, Science, 241, 1473–1475, 1988.

Chaves, M. M., Pereira, J. S., Maroco, J., Rodrigues, M. L., Ricardo, C. P. P., Osorio, M. L., Carvalho, I., Faria, T., and Pinheiro, C.: How plants cope with water stress in the field. Photosynthesis and growth, Ann. Bot., 89, 907–916, 2002.

Chaxel, E. and Chollet, J.P.: Ozone production from Grenoble city during the August 2003 heatwave, Atmos. Env., 43, 4784-4792, 2009.

Chen, F., and Dudhia, J.: Coupling an advanced land surface-hydrology model with the Penn State-NCAR MM5 modeling system, Part I: Model implementation and sensitivity, Mon. Weather Rev., 129, 569–585, 2001.

~~Funk, J.~~Curci, G., Beekmann, M., Vautard, R., Siamek, G., Steinbrecher, R., Theloke, J. and Friedrich, R.: Modeling study of the impact of isoprene and terpene biogenic emissions on European ozone levels, Atmos. Env., 43, 7, 1444-1455, 2009.Funk, J. L., Mak, J. E., and Lerdau, M. T.: Stress-induced changes in carbon sources for isoprene production in *Populus deltoides*, Plant Cell Environ., 27, 747–755, 2004.

Genard-Zielinski, A. C., Ormeño, E., Boissard, C., and Fernandez, C.: Isoprene emissions from Downy Oak under water limitation during an entire growing season: what cost for growth? PLoS ONE, 9 (11): e112418. doi:10.1371/journal.pone.0112418, 2014.

Genard-Zielinski, A. C., Boissard, C., Fernandez, C., ~~Boissard, C.,~~ Kalokridis, C., ~~Gros, V.,~~ Lathière, J., ~~Orts, JP., Greff, S~~Gros, V., Bonnaire, N., and Ormenõ, E.: Variability of BVOC emissions from a Mediterranean mixed forest in southern France with a focus on *Quercus pubescens*, ACP~~., 14, 17225–17261~~, 15, 431-446, 2015.

Geron, C., Guenther, A. B., Sharkey, T., and Arnts, R. R.: Temporal variability in basal isoprene emission factor, Tree Physiol., 20, 799–805, 2000.

Formatted: Font: Italic

Formatted: Font: Italic

Giorgi, F. and Lionello, P.: Climate change projections for the Mediterranean region, Global Planet. Change, 63, 90–104, 2008.

Goldstein, A. and Steiner, A. H.: Biogenic VOCs, in: Volatile Organic Compounds in the Atmosphere, Koppmann R., (Ed), Blackwell Publishing Ltd, Oxford, UK, 82-128, 2007.

Grinspoon, J., Bowman, W. D., and Fall, R.: Delayed onset of isoprene emission in developing velvet bean (Mucuna sp.) leaves, Plant Physiol., 97, 170–174, 1991.

Grote, R., Morfopoulos, C., Niinemets, U., Sun, Z., Keenan, T. F., Pacifico, F., and Butler, T.: A fully integrated isoprenoid emissions model coupling emissions to photosynthetic characteristics, Plant Cell Environ., 37, 1965–1980, 2014.

Guenther, A. B., Hewitt, C. N., and Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global-model of natural volatile organic-compound emissions, J. Geophys. Res-Atmos., 100, 8873–8892, 1995.

Guenther, A. B., Karl, T., Harley, P., Wiedinmyer, C., Palmer., PI, and Geron, C. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), ACP., 6, 3181–3210, 2006a.

Guenther, A. B., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability - Observations with Eucalyptus and emission rate algorithm development, J. Geophys. Res-Atmos., 96, 10799–10808, 1991.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and Monoterpene Emission Rate Variability - Model Evaluations and Sensitivity Analyses, J. Geophys. Res-Atmos., 98, 12609–12617, 1993.

Guimberteau, M., Ronchail, J., Espinoza, J. C., Lengaigne, M., Sultan, B., Polcher, J., Drapeau, G., Guyot, J. L., Ducharne, A., and Ciais, P.: Future changes in precipitation and impacts on extreme streamflow over Amazonian sub-basins, Environ. Res. Lett., 8(1), 014040, 2013.

Hakola, H., Rinne, J., and Laurila, T.: The hydrocarbon emission rates of tea-leafed willow (Salix phylicifolia), silver birch (Betula pendula) and European aspen (Populus tremula), Atmos. Environ., 32, 1825–1833, 1998.

IPCC Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Stocker, T. F., Qin, D., Plattner, G. K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., (Eds), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535pp., 2013.

Keenan, T., Niinemets, U., Sabate, S., Gracia, C., and Peñuelas, J.: Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties, ACP~~.~~, 9, 4053–4076, 2009.

Köstner, B., Matyssek, R., Heilmeier, H., Clausnitzer, F., Nunn, A. J., and Wieser, G.: Sap flow measurements as a basis for assessing trace-gas exchange of trees, Flora, 203, 14–33, 2008.

Krinner, G., Viovy, N., de Noblet-Ducoudre, N., Ogee, J., Polcher, J., Friedlingstein, P., Ciais, P., Sitch, S., and Prentice, I.: A dynamic global vegetation model for studies of the coupled atmosphere-biosphere system, Global Biogeochem. Cy~~.~~, 19, GB1015, 2005.

Formatted: Default Paragraph Font, French (France)

Lavoir, A.V., Staudt, M., Schnitzler, J.P., Landais, D., Massol, F., Rocheteau, A., Rodriguez, R., Zimmer, I., and Rambal, S.: Drought reduced monoterpene emissions from the evergreen Mediterranean oak *Quercus ilex* : results from a throughfall displacement experiment, Biogeosciences, 6, 1167-1180, 2009.

Lichtenthaler, H. K., Schwender, J., Disch, A., and Rohmer, M.: Biosynthesis of isoprenoids in higher plant chloroplasts proceeds via a mevalonate-independent pathway, FEBS Lett., 400, 271–274, 1997.

Llusià, J., Peñuelas, J., Alessio, G., and Estiarte, M.: Contrasting species - specific, compound - specific, -seasonal- and interannual responses of foliar isoprenoid emissions to experimental drought in a Mediterranean shrubland, Int. J. Plant Sci., 169, 637–645, 2008.

Loreto, F. and Fineschi, S.: Reconciling functions and evolution of isoprene emission in higher plants, New Phytol., 206, 578–582, 2015.

Loreto, F. and Schnitzler, J-P.: Abiotic stresses and induced BVOCs, Trends Plant Sci., 15, 154–166, 2010.

Monson, R. K., Harley, P. C., Litvak, M. E., Wildermuth, M., Guenther, A. B., Zimmerman, P. R., and Fall, R.: Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves, Oecologia, 99, 260–270, 1994.

Müller, J.F., Stavrakou, T., Wallens, S., De Smelt, I., Van Roozendael, M., Potosnak, M.J., Rinne, J., Munger, B., Goldstein, A and Guenther, A.B. Global isoprene emission estimated using MEGAN, ECMWF analyses and a detailed canopy environmental model, Atmos. Phys. Chem., 8, 2008.

Owen, S., Boissard, C., Hagenlocher, B., and Hewitt, C.: Field studies of isoprene emissions from vegetation in the Northwest Mediterranean region, J. Geophys. Res., 103, 25499–25511, 1998.

Pacifico, F., Harrison, S. P., Jones, C. D., and Sitch, S.: Isoprene emissions and climate, Atmos. Environ., 43, 6121–6135, 2009.

Formatted: Default Paragraph Font, French (France)

Pegoraro, E., Rey, A., ~~Greenberg, J., Harley, P. C., Grace, J., Malh~~Malhi, Y., Bobich, E., Barron-Gafford, G., Grieve, A., and ~~Guenther, A. B~~Murthy, R.: Effect of ~~drought~~CO2 concentration and vapour pressure deficit on isoprene emission ~~rates~~ from leaves of ~~Quercus virginiana Mill, Atmos. Environ., 38, 6149-6156~~*Populus deltoides* during drought, Functionnal Plant Biology, 31 (12) 1137–1147, 2004.

Peñuelas, J., Llusià, J., Asensio, D., Munné-Bosch, S., Linking isoprene with plant thermotolerance, antioxidants, and monoterpene emissions, Plant Cell Environ., 28, 278-286, 2005.

Peñuelas, J. and Staudt, M.: BVOCs and global change, Trends Plant Sci., 15, 133–144, 2010.

Petron, G., Harley, P. C., Greenberg, J., and Guenther, A. B.: Seasonal temperature variations influence isoprene emission, Geophys. Res. Lett., 28, 1707–1710. 2001.

Polade, S. D., Pierce, D. W., Cayan, D. R., Gershunov, A., and Dettinger, M. D.: The key role of dry days in changing regional climate and precipitation regimes, Sci. Rep., 4, 4364, 2014.

Formatted: Default Paragraph Font, French (France)

Potosnak, M. J., LeStourgeon, L., Pallardy, S. G., Hosman, KP., Gu, L., Karl, T., Geron, C., and Guenther, A. B.: Observed and modeled ecosystem isoprene fluxes from an oak-dominated temperate forest and the influence of drought stress, Atmos. Environ., 84, 314–322, 2014.

Rodriguez-Calcerrada, J., Buatois, B., Chiche, E., Shahin, O., and Staudt, M.: Leaf isoprene emission declines in Quercus pubescens seedlings experiencing drought - Any implication of soluble sugars and mitochondrial respiration? Environ. Exp. Bot., 85, 36–42, 2013.

Santonja, M., Fernandez, C., Gauquelin, T., and Baldy, V.: Climate change effects on litter decomposition: intensive drought leads to a strong decrease of litter mixture interactions, Plant Soil, 393, 69-82, 2015.

Saunier, A., Ormeño, E., Boissard, C., Wortham, H., Temime-Roussel, B., Lecareux, C., Armengaud, A., and Fernandez, C.: Effect of mid-term drought ~~on~~ *Quercus pubescens* BVOCs emission seasonality ~~in Quercus pubescens~~ and their ~~dependence to light~~dependency onlight and/or temperature, ~~ACP, in review~~Atmos. Chem. Phys. 17, 7555-7566, 2017.

Sharkey, T. D., and Loreto, F.: Water-stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves, Oecologia, 95, 328–333, 1993.

Simon, V., Dumergues, L., Solignac, G., and Torres, L.: Biogenic emissions from Pinus halepensis: a typical species of the Mediterranean area, Atmos. Environ., 74, 37–48, -2005.

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C.N., Janson, R., Khalil, M.A.K., Owen, S., Pierce, T.E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrasón, L., and Öquist, M.G.: Inventorying emissions from nature in Europe, J. Geophys. Res-Atmos., 104, 8113–8152. doi:10.1029/98jd02747, 1999.

Tani, A., Tozaki, D., Okumura, M., Nozoe, S., and Hirano, T.: Effect of drought stress on isoprene emission from two major Quercus species native to East Asia. Atmos. Environ., 45, 6261–6266, 2011.

Tognetti, R., Longobucco, A., Miglietta, F., and Raschi, A.: Transpiration and stomatal behaviour of Quercus ilex plants during the summer in a Mediterranean carbon dioxide spring, Plant Cell Environ., 21, 613-622, 1998.

Velikova, V., Sharkey, T. D., and Loreto, F.: Stabilization of thylakoid membranes in isoprene-emitting plants reduces formation of reactive oxygen species, Plant Signal. Behav., 7, 139–141, 2012.

Voncaemmerer, S. and Farquhar, G. D.: Some relationships between the biochemistry of photosynthesis and the gas-exchange of leaves, Planta, 153, 376–387, 1981.

von Kuhlmann, R., Lawrence, M.G., Pöschl, U. and Crutzen, P.J.: Sensitivities in global scale modelling of isoprene, Atmos. Chem. Phys., 4, 1-17, 2004.

Warszawski, L., Frieler, K., Huber, V., Piontek, F., Serdeczny, O., and Schewe, J.: The Inter-Sectoral Impact Model Intercomparison Project (ISI-MIP): Project framework, –PNAS., 111, 3228–3232, 2014.

Wiberley, A., Linskey, A., Falbel, T., and Sharkey, T.: Development of the capacity for isoprene emission in kudzu, Plant, Cell Environ., 28, 898–905, 2005.

Zheng, Y., Unger, N., Barkley, M. P., and Yue, X.: Relationships between photosynthesis and formaldehyde as a probe of isoprene emission, ACP~~.,~~, 15, 8559–8576, 2015.

Zobler, L.: A world soil file for global climate modelling, NASA Technical Memorandum, NASA 87802, New York, U.S.A, 1986.

Figure caption

Figure 1~~.~~: Seasonal variations of daily environmental parameters measured at the O_3HP from March 2012 to ~~July~~June 2013. (**a**) Ambient air temperature *T* was obtained at 6.5 m above ground level (a.g.l.), approximately 1.5 m above the canopy. (**b**) Photosynthetic active radiations PAR received at 6.5 m a.g.l. in the ND plot. (**c**) Cumulated precipitation P_{cum} measured over the ND (blue) and AD (red) plot. (**d**) Mean soil water content SW ± SD measured at -0.1 m depth from various soil probes in the ND (blue, *n*=3) and AD (red, *n*=5) plot.

Figure 2~~.~~: Seasonal variations of monthly *Q. pubescens* gas exchanges observed at O_3HP (June 2012 to June 2013) under ND (blue) and AD (red) (mean ± SD). (**a**) Stomatal conductance to water vapour G_w. (**b**) Net photosynthetic assimilation P_n. (**c**) Measured branch isoprene emission rate ER. (d) Isoprene emission factor (I_s) calculated according to Guenther et al. (~~1993~~1995) using *in situ* ER *vs* $C_L \times C_T$ correlations, except in July where mean ER measured under enclosure conditions close to 1000 µmol m^{-2} s^{-1} and 30 °C was used. Differences between ND and AD using Mann-Whitney U-tests are denoted using lower case letters (a>b>c>d). Differences among ~~months~~water treatment stress using Kruskal-wallis tests are denoted by asterisks (*: P<0.05; **: P<0.01; ***: P<0.001).

Figure 3: ~~Calculated *vs*~~ Comparison between isoprene emission rates (in µgC g_{DM}^{-1} h^{-1}) calculated using MEGAN2.1 (ER_{MEGAN}, Guenther et al., 2012) and measured isoprene emission rates (ER) versus the wilting point value θw (0.005 to 0.15 m^3 m^{-3}), from June 2012 to June 2013, under (**a**) ND (~~blue,~~ *n*=267) and ~~AD (red, *n*=138); from June 2012 to 2013, using (a) the MEGAN~~(**b**) AD (*n*=138). Since the rain exclusion device was only implemented soon prior to our study's commencement in June 2012, the ND and AD measurements were considered together for June 2012. Linear regressions for ND June 2012 were: y=1.13x-12.05, R^2=0.80 (θw=0.05 m^3 m^{-3}); y=1.13x-7.13, R^2=0.80 (θw=0.1 m^3 m^{-3}); y=1.12x-16.94, R^2=0.76 (θw=0.15 m^3 m^{-3}). The dotted line is the 1:1 line.

Figure 4: Ratio between observed (ER) and calculated (ER_{MEGAN}) isoprene emission rates versus the soil water content SW measured at the O_3HP, under (**a**) ND (*n*=267) and, (**b**) AD (*n*=138). Given that the rain exclusion device was only implemented just before our study

Formatted: English (U.K.)

Formatted: Font: Not Bold, English (U.K.)

Formatted: Heading 1, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Bold

Formatted: Font: Not Italic

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted ...

Formatted: Font color: Text 1

began in June 2012, the ND and AD measurements were considered together for June 2012. The dotted line is for SW=*θ*w measured at O$_3$HP (0.15 m^3 m^{-3}).

Figure 5: Calculated versus measured isoprene emission rates (in µgC g$_{DM}$$^{-1}$ h^{-1}) under ND (*n*=267) and AD (*n*=138) from June 2012 to June 2013, using (**a**) *G*14 (this study) and (**b**) MEGAN2.1 isoprene model (Guenther et al~~. 2006~~., 2012) with a wilting point value *θ*w of 0.~~138 m^3 m^{-3} (Chen et Dudhia, 2001) and an isoprene emission fator (I_s) of 53 µgC g$_{DM}$$^{-1}$ h^{-1} (Simpson *et al.*, 1999), and, (b) the isoprene emission algorithm *G*14 developped in this study; the linear regression relation is given together with the correlation coefficient R²; dotted line is~~15 m^3 m^{-3} (measured at the O$_3$HP). The dotted line is the 1:1 line.

Figure ~~4.~~:6: Seasonal variations of the relative contribution ~~on isoprene emission rates (ER) of (a) the environmental parameters used in *G*14 (the received incident PAR *L*, air temperature *T*, soil water content SW, soil temperature ST and precipitation *P*) whatever their frequencies considered in *G*14; and, of (b) the~~ of the different frequencies as considered in *G*14 (0, 7, 14, 21 days before the measurement), whatever the ~~environmental parameters in *G*14.~~regressors x_i, under (**a**) ND (*n*=267) and (**b**) AD (*n*=138).

Figure ~~5.: Present~~7: Seasonal variations between present (2000-2010) ~~to~~and future (2090-2100) relative changes ~~in the seasonal variations~~of SW, *P* , ST and *T* over the continental Mediterranean area obtained using (**a**) RCP2.6 ~~(left)~~ and (**b**) RCP8.5 ~~(right)~~ projections.

Figure 8: Sensitivity of the seasonal variation of isoprene emission rates calculated using *G*14 (ER$_{G14}$, in µgC g$_{DM}$$^{-1}$ h^{-1}, this study) to (**a**) *T* and ST changes as in RCP2.6 (‘T’ case) and RCP8.5 (‘TT’ case) respectively; (**b**) SW and *P* changes as in RCP2.6 (‘P’ case) and RCP8.5 (‘PP’ case) respectively; and (**c**) combined *T*, ST, *P* and SW changes as in RCP2.6 (‘T+P’ case) and RCP8.5 (‘TT+PP’ case) respectively. Present and future cases were calculated for (~~a) monthly precipitation (*P*, mm), air temperature (*T*, °C), soil temperature (ST, °C) and~~ 2000-2010) and (2090-2100) respectively. Overall annual relative changes to present are framed.

Formatted: Font: Not Italic

Formatted: Font color: Text 1

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font: Not Bold, Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Figure 9: Sensitivity of the seasonal variation of isoprene emission rates calculated using *G*14 (ER_{G14}, in µgC g_{DM}^{-1} h^{-1}) to SW. Overall annual relative changes to present (2000-2010) are framed.

Table caption

Table 1: Correlations between ER_{MEGAN}/ER and the soil water content (SW~~, L_{H2O} L_{soil}^{-1}); (b) monthly ER~~) cumulated over 7 to 21 days before the measurement. ER_{MEGAN} and ER are isoprene emission rates calculated using MEGAN2.1 (Guenther et al., 2012) and measured (this study) respectively.

Table 2: Annual absolute ~~changes assessed using *G*14 (*d*ER_{G14}) from March to October; (c) monthly ER relative changes assessed using *G*14 from March to October; (d) the relative impact of temperature (as the sum of *T* and ST, in blue) and water availability (as the sum of P and SW, in red) on ER_{G14} relative change; and, (e), the~~and relative ~~impact~~changes to present of ~~different frequencies (instantaneous and cumulated over 7, 14 and 21 days) on ER_{G14} relative change. Inserted numbers are mean annual values~~SW, *P*, ST and *T* according to RCP2.6 and RCP8.5 scenarios. Present and future cases were calculated for (2000-2010) and (2090-2100) respectively.

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Left, Space Before: 0 pt, After: 10 pt

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: Font color: Text 1

Formatted: English (U.S.)

Formatted: Font: Times, Font color: Text 1

~~Appendice~~Appendix 1: Calculation of isoprene emission rates ~~ER~~ER$_{G14}$ (µgC ~~g$_{DW}$~~g$_{DM}$$^{-1}$ h^{-1}) using the *G*14 algorithm

Due to the large range of ER variations, emissions were considered as logER, where~~-~~:

~~logER~~logER$_{G14}$=log[~~ER~~ER$_{G14\,(CN)}$]×*s* + *m* and *s* is the standard deviation of ~~log de ER (xx~~logER$_{G14}$ (s=0.8916), *m* is the mean of ~~logER (xx~~logER$_{G14}$ (m=0.8434), log[ER$_{G14\,(CN)}$] the central-normalised log10 of ER$_{G14}$ calculated as:

log[~~ER~~ER$_{G14(CN)}$]$=w_0 + w_{1,k} \times \tanh(N_1) + w_{2,k} \times \tanh(N_2) + w_{3,k} \times \tanh(N_3)$

where $$N_1 = w_{0,1} + \sum_{i=1}^{i=16}\sum_{j=1}^{j=16} w_{i,1} \times x_j$$

$$N_2 = w_{0,2} + \sum_{i=1}^{i=16}\sum_{j=1}^{j=16} w_{i,2} \times x_j$$

$$N_3 = w_{0,3} + \sum_{i=1}^{i=16}\sum_{j=1}^{j=16} w_{i,3} \times x_j$$

Table A1. The optimised weights *w* as follows:

w0	-1.29837907				
w0,1	-0,16226148	*w0,2*	2.90404784	*w0,3*	0.23868843
w1,1	0.07736039	*w1,2*	2.18450515	*w1,3*	-0.1283214
w2,1	0.04806346	*w2,2*	-0.0074737	*w2,3*	0.06711214
w3,1	-0.32907201	*w3,2*	0.31067189	*w3,3*	0.14496404
w4,1	0.54847219	*w4,2*	0.40895098	*w4,3*	-1.1895104
w5,1	-0.03820985	*w5,2*	0.27886813	*w5,3*	0.35561345
w6,1	0.34677986	*w6,2*	0.2906721	*w6,3*	-2.84020867
w7,1	-1.44104866	*w7,2*	-1.23651445	*w7,3*	4.30350692
w8,1	-0.63559865	*w8,2*	-0.63879809	*w8,3*	3.61172683
w9,1	0.81398482	*w9,2*	0.85053882	*w9,3*	0.46501183
w10,1	-2.01376339	*w10,2*	1.59664603	*w10,3*	-0.74513053
w11,1	1.61737626	*w11,2*	-1.68773125	*w11,3*	-2.29893094
w12,1	-0.57093409	*w12,2*	-0.76488022	*w12,3*	1.96571085
w13,1	0.78483127	*w13,2*	0.9786783	*w13,3*	-1.88733755
w14,1	0.05311514	w14,2	-0.88244467	w14,3	-1.90110521
w15,1	-0.47856411	w15,2	-0.88883049	w15,3	1.35713546
w16,1	0.39618491	*w16,2*	0.55564983	*w16,3*	-0.73830992
w1,k	-2.22601227	*w2,k*	-1.64346181	*w3,k*	-1.32117586

Formatted: Font color: Text 1, English (U.K.)

Formatted: Heading 1, Left, Space Before: 0 pt, After: 0 pt, Line spacing: single

Formatted: English (U.K.)

Formatted: English (U.K.)

Formatted: Font: Not Bold, English (U.K.)

Formatted: Space After: 6 pt

Formatted: Font color: Auto

Formatted: Font color: Auto

Formatted: Font: Italic, Subscript

Formatted: Font: Italic, Subscript

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Table A2. The selected input regressors x_i as follows:

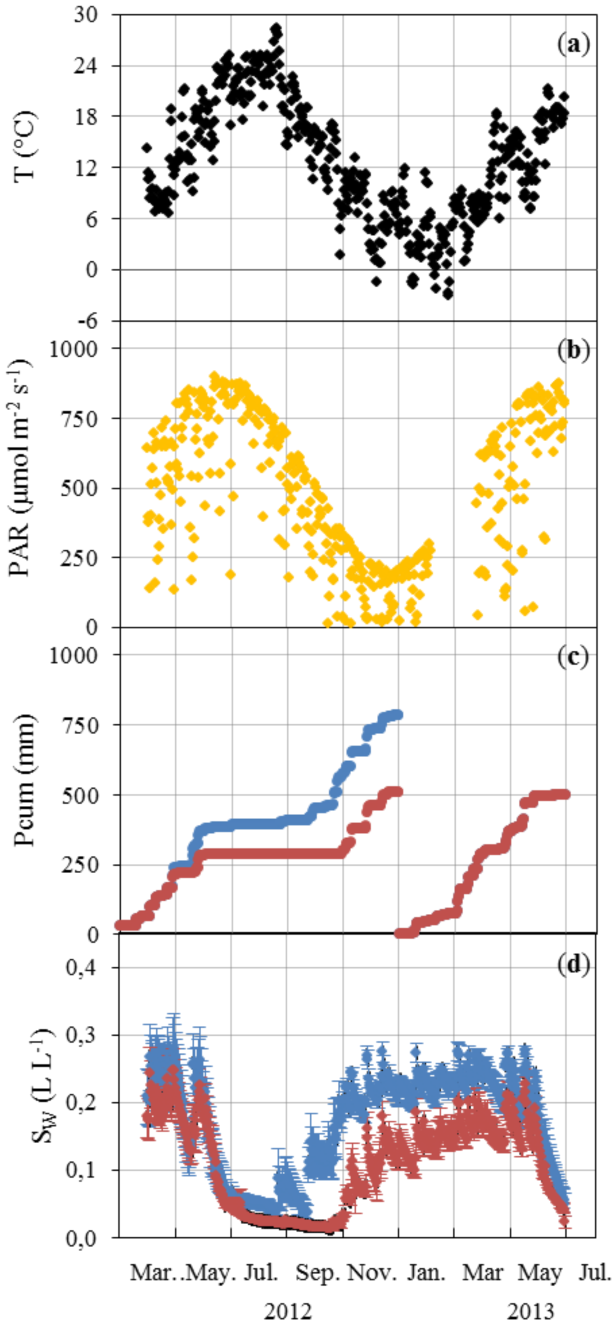
x_1	$L0$
x_2	L-1
x_3	$T0$
x_4	T-1
x_5	T_{M}-T_{m}
x_6	T-14
x_7	T-21
x_8	SW-1
x_9	SW-7
x_{10}	SW-14
x_{11}	SW-21
x_{12}	ST-7
x_{13}	ST-14
x_{14}	P-7
x_{15}	P-14
x_{16}	P-21

Formatted: Font: Not Bold

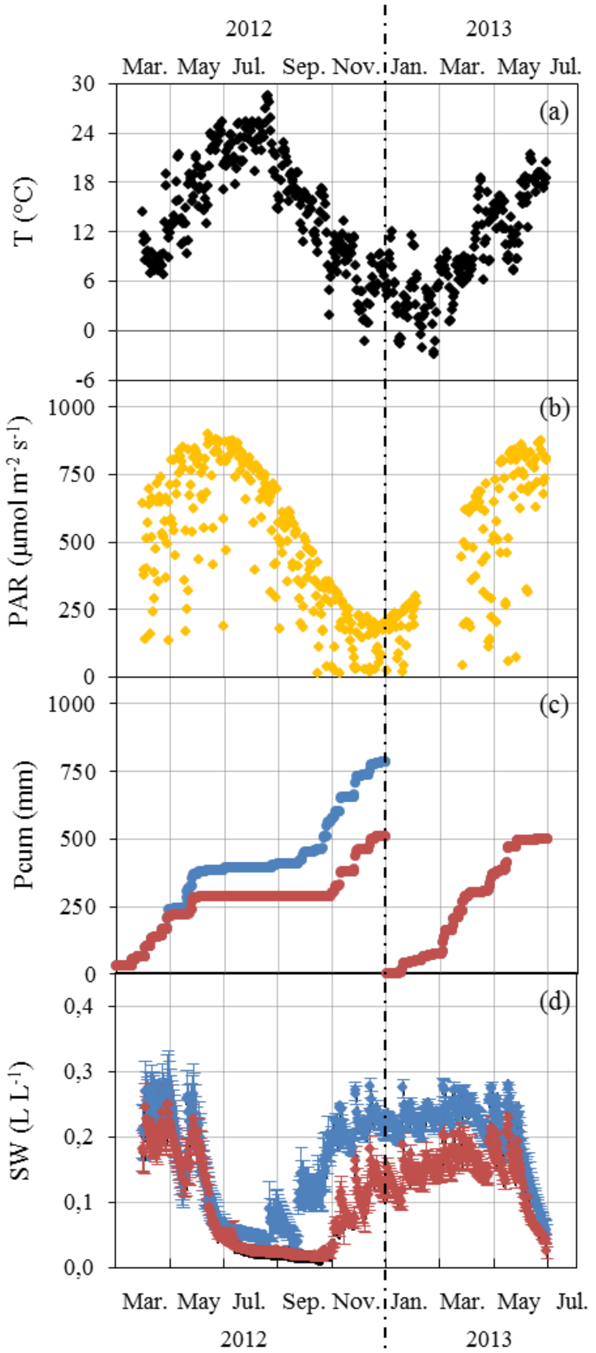
Formatted: Font: Bold

Formatted: Left, Space Before: 0 pt, After: 8 pt, Line spacing: Multiple 1.08 li

Figure 1

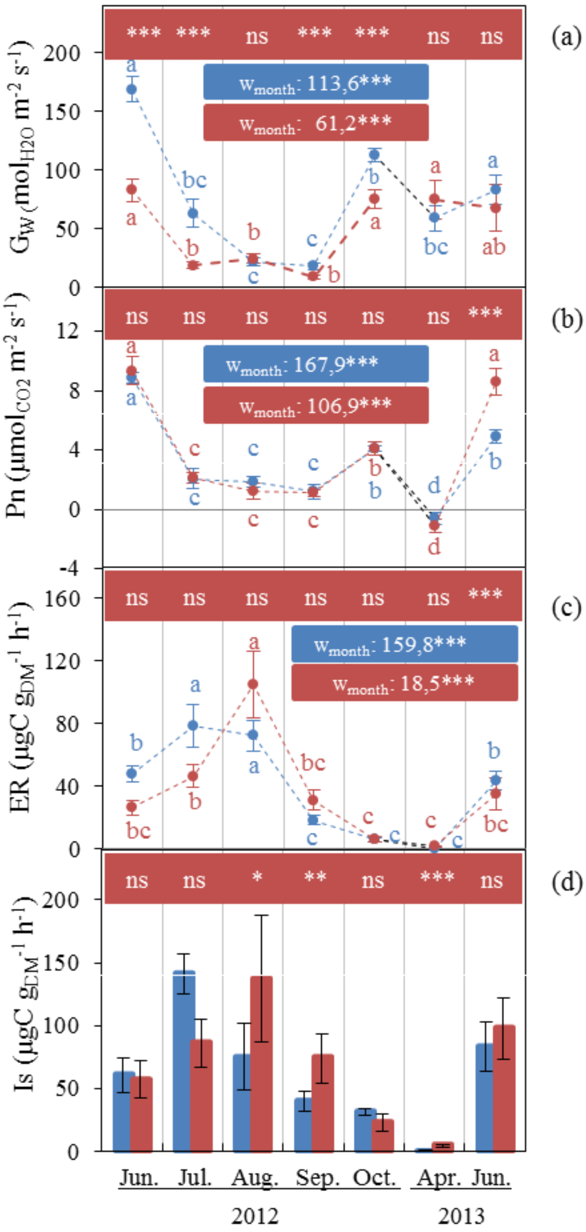


T (°C)
30
24
18
12
6
0
-6
(a)
PAR (µmol m-2 s-1)
1000
750
500
250
0
(b)
Pcum (mm)
1000
750
500
250
0
(c)
SW (L L-1)
0,4
0,3
0,2
0,1
0,0
(d)
Mar.
May.
Jul.
Sep.
Nov.
Jan.
Mar
May
Jul.
2012
2013


2012
2013
Mar. May Jul. Sep. Nov. Jan. Mar. May Jul.
T (°C)
30
24
18
12
6
0
-6
(a)
PAR (µmol m-2 s-1)
1000
750
500
250
0
(b)
Pcum (mm)
1000
750
500
250
0
(c)
SW (L L-1)
0,4
0,3
0,2
0,1
0,0
(d)
Mar. May Jul. Sep. Nov. Jan. Mar. May Jul.
2012
2013

Formatted: Font: Bold

Figure 2



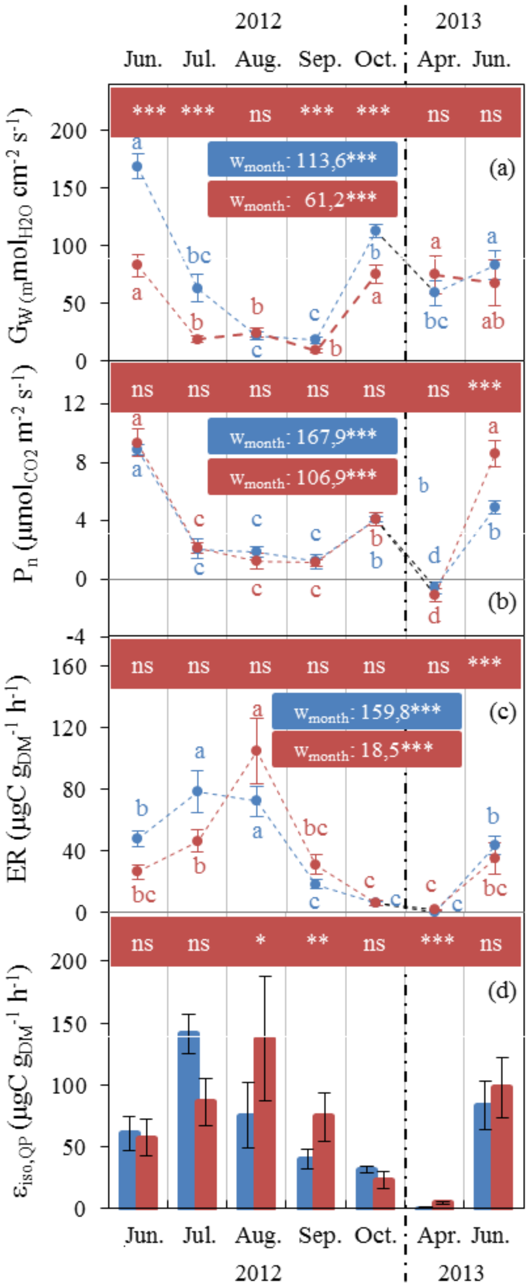
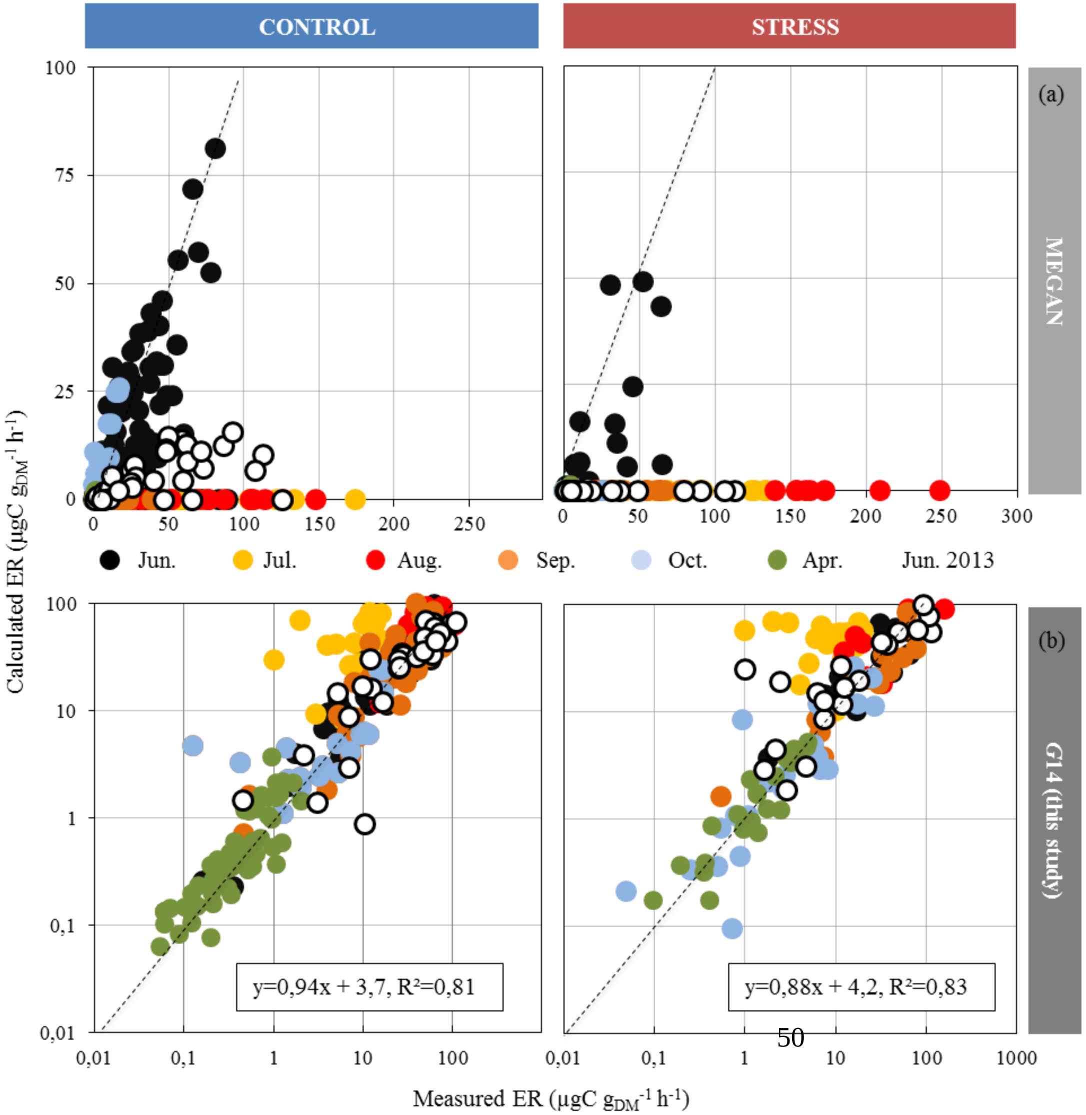

2012
2013
Jun. Jul. Aug. Sep. Oct. Apr. Jun.
*** *** ns *** *** ns ns
G_W (mmol_H2O cm-2 s-1)
200
150
100
50
0
W_month: 113,6***
W_month: 61,2***
(a)
a a bc b b c c b b a a a bc a ab
ns ns ns ns ns ns ***
P_n (µmol_CO2 m-2 s-1)
12
8
4
0
-4
W_month: 167,9***
W_month: 106,9***
(b)
a a c c c c c c b b b d d a b
ns ns ns ns ns ns ***
ER (µgC g_DM-1 h-1)
160
120
80
40
0
W_month: 159,8***
W_month: 18,5***
(c)
b bc a b a a bc c c c c c b bc
ns ns * ** ns *** ns
ε_iso,QP (µgC g_DM-1 h-1)
200
150
100
50
0
(d)
Jun. Jul. Aug. Sep. Oct. Apr. Jun.
2012
2013

Figure 3

Formatted: Left, Space Before: 0 pt, After: 8 pt, Line spacing: Multiple 1.08 li


CONTROL
STRESS
(a)
MEGAN
(b)
G14 (this study)
Calculated ER (µgC gDM-1 h-1)
Measured ER (µgC gDM-1 h-1)
● Jun.
● Jul.
● Aug.
● Sep.
● Oct.
● Apr.
Jun. 2013
y=0,94x + 3,7, R²=0,81
y=0,88x + 4,2, R²=0,83
0
25
50
75
100
0
50
100
150
200
250
300
0,01
0,1
1
10
100
1000

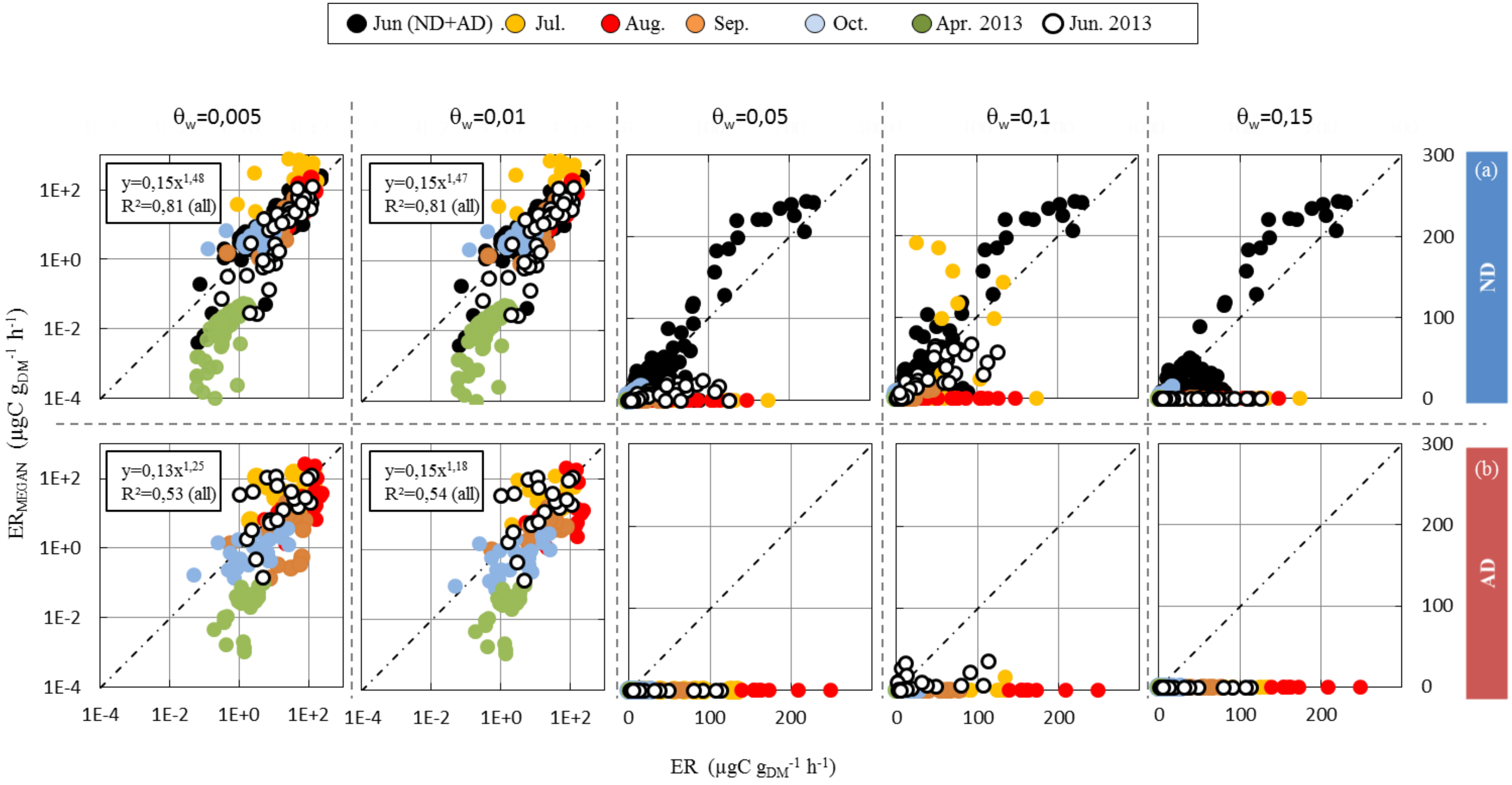
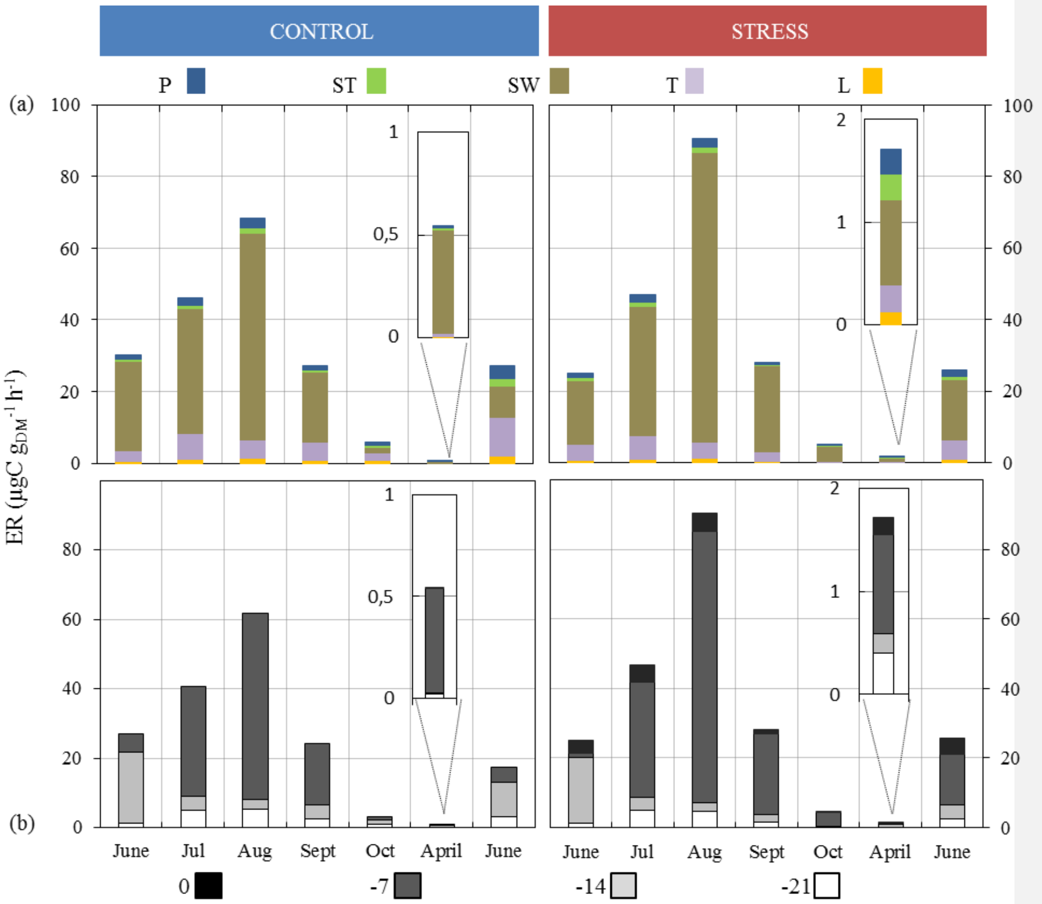
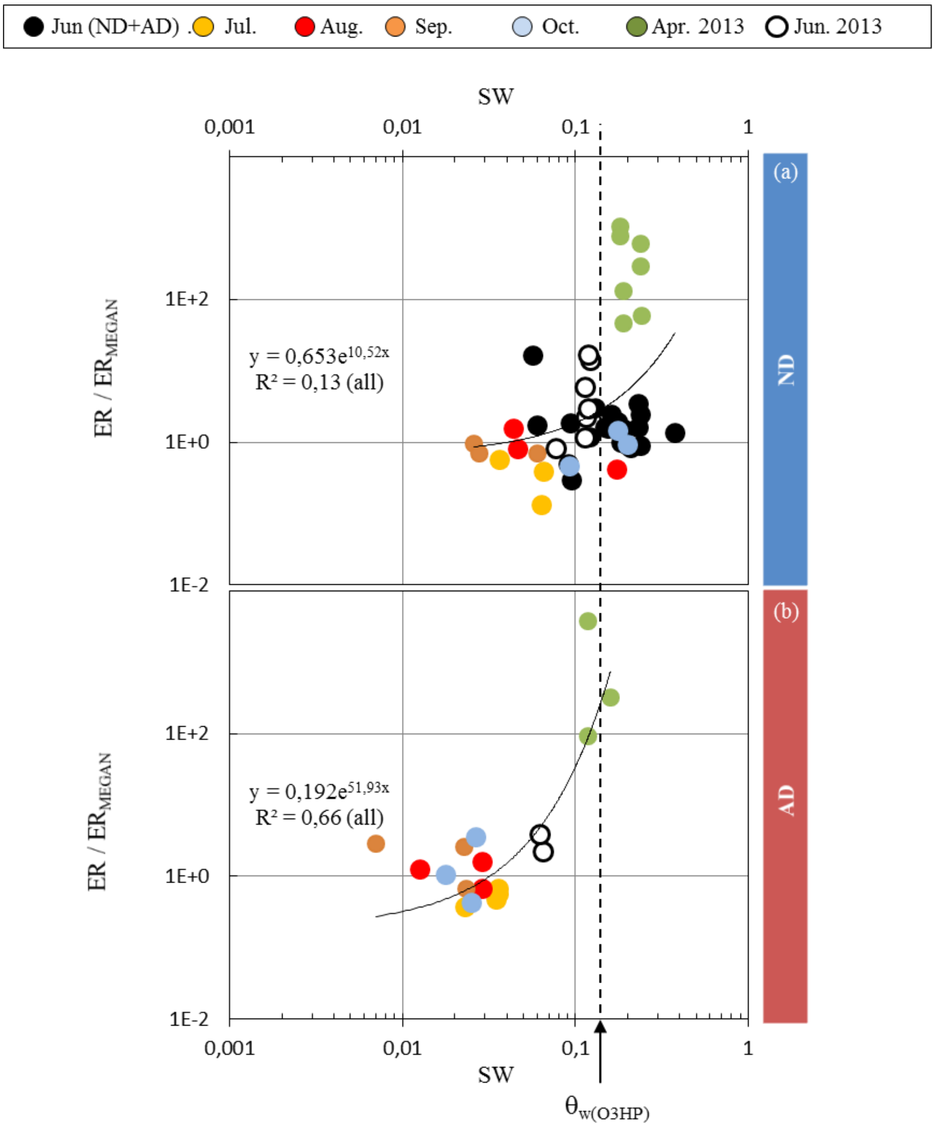

● Jun (ND+AD)
● Jul.
● Aug.
● Sep.
● Oct.
● Apr. 2013
○ Jun. 2013
θw=0,005
θw=0,01
θw=0,05
θw=0,1
θw=0,15
y=0,15x1,48
R²=0,81 (all)
y=0,15x1,47
R²=0,81 (all)
y=0,13x1,25
R²=0,53 (all)
y=0,15x1,18
R²=0,54 (all)
1E+2
1E+0
1E-2
1E-4
300
200
100
0
(a)
ND
(b)
AD
ERMEGAN (µgC gDM-1 h-1)
1E-4
1E-2
1E+0
1E+2
0
100
200
ER (µgC gDM-1 h-1)

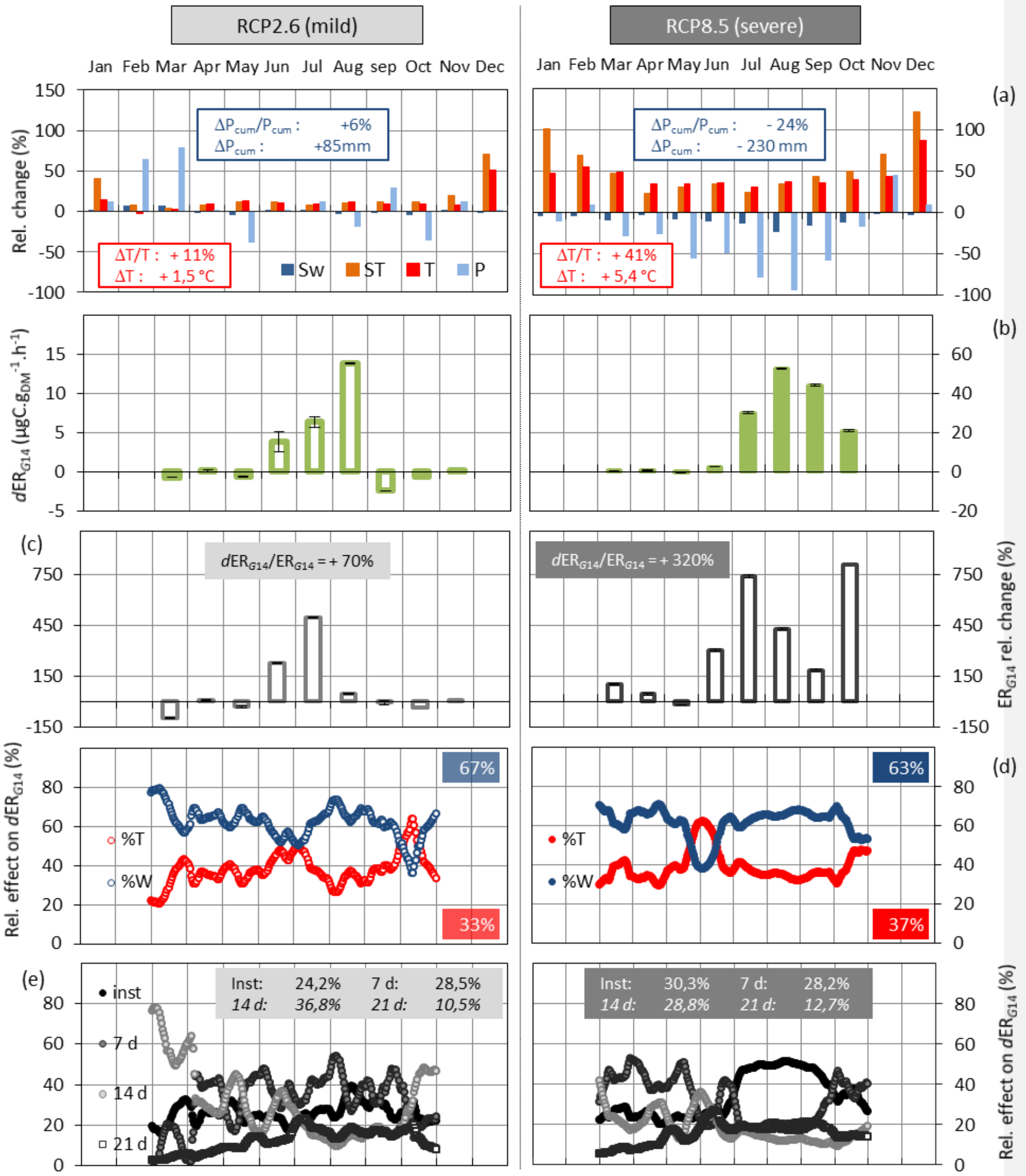
Figure 4


CONTROL
STRESS
P
ST
SW
T
L
(a)
(b)
ER (µgC gDM-1 h-1)
100
80
60
40
20
0
1
0,5
0
2
1
0
June
Jul
Aug
Sept
Oct
April
June
0
-7
-14
-21



Formatted: Indent: Left: -2.25 cm

Figure 5


RCP2.6 (mild)
RCP8.5 (severe)
Jan Feb Mar Apr May Jun Jul Aug sep Oct Nov Dec
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
(a)
Rel. change (%)
150
100
50
0
-50
-100
ΔP_cum/P_cum : +6%
ΔP_cum : +85mm
ΔT/T : + 11%
ΔT : + 1,5 °C
Sw
ST
T
P
ΔP_cum/P_cum : - 24%
ΔP_cum : - 230 mm
ΔT/T : + 41%
ΔT : + 5,4 °C
(b)
dER_G14 (µgC.g_DM^-1.h^-1)
15
10
5
0
-5
60
40
20
0
-20
(c)
dER_G14/ER_G14 = + 70%
dER_G14/ER_G14 = + 320%
750
450
150
-150
ER_G14 rel. change (%)
(d)
Rel. effect on dER_G14 (%)
80
60
40
20
0
%T
%W
67%
33%
63%
37%
(e)
inst
7 d
14 d
21 d
Inst: 24,2% 7 d: 28,5%
14 d: 36,8% 21 d: 10,5%
Inst: 30,3% 7 d: 28,2%
14 d: 28,8% 21 d: 12,7%
Rel. effect on dER_G14 (%)

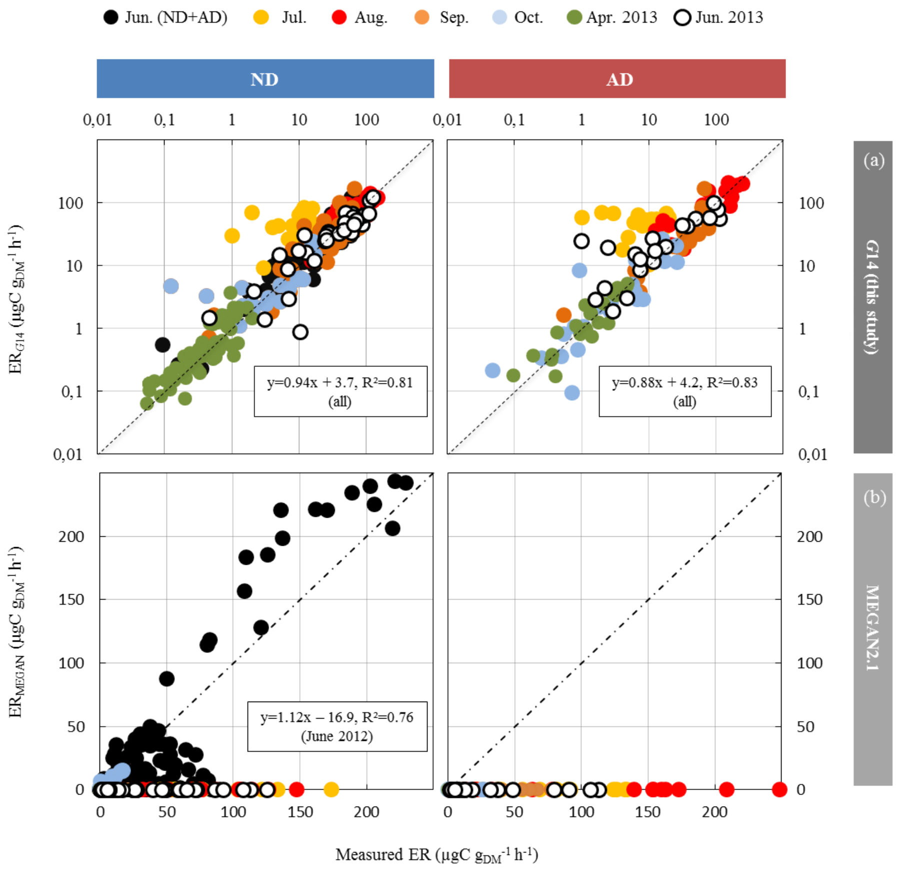

● Jun. (ND+AD) ● Jul. ● Aug. ● Sep. ● Oct. ● Apr. 2013 ○ Jun. 2013
ND
AD
0,01 0,1 1 10 100
0,01 0,1 1 10 100
100
10
1
0,1
0,01
ER_{G14} (µgC g_{DM}^{-1} h^{-1})
y=0.94x + 3.7, R²=0.81
(all)
y=0.88x + 4.2, R²=0.83
(all)
(a)
G14 (this study)
200
150
100
50
0
ER_{MEGAN} (µgC g_{DM}^{-1} h^{-1})
y=1.12x – 16.9, R²=0.76
(June 2012)
(b)
MEGAN2.1
0 50 100 150 200
0 50 100 150 200
Measured ER (µgC g_{DM}^{-1} h^{-1})

Figure 6

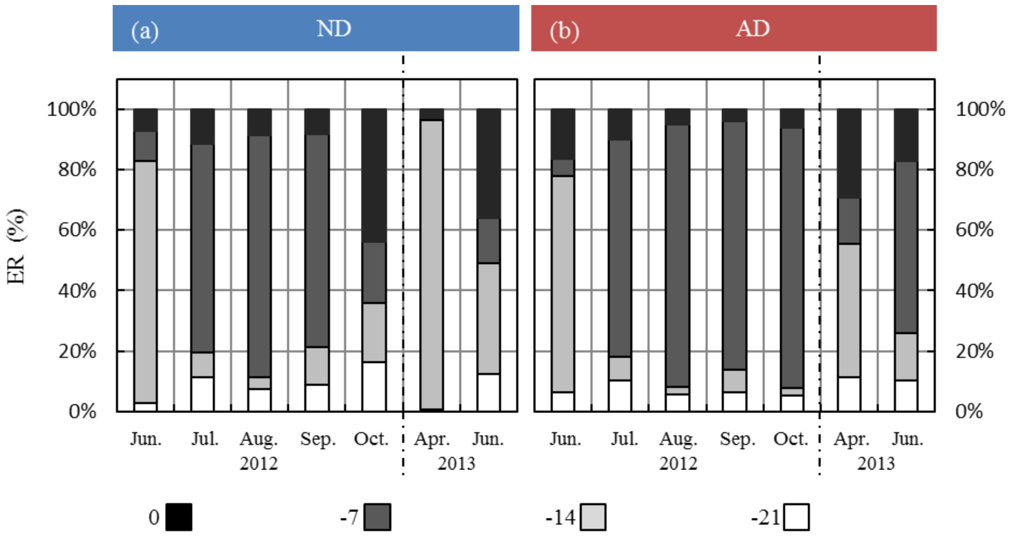

(a)
ND
(b)
AD
ER (%)
100%
80%
60%
40%
20%
0%
Jun.
Jul.
Aug.
Sep.
Oct.
2012
Apr.
Jun.
2013
0
-7
-14
-21

Figure 7

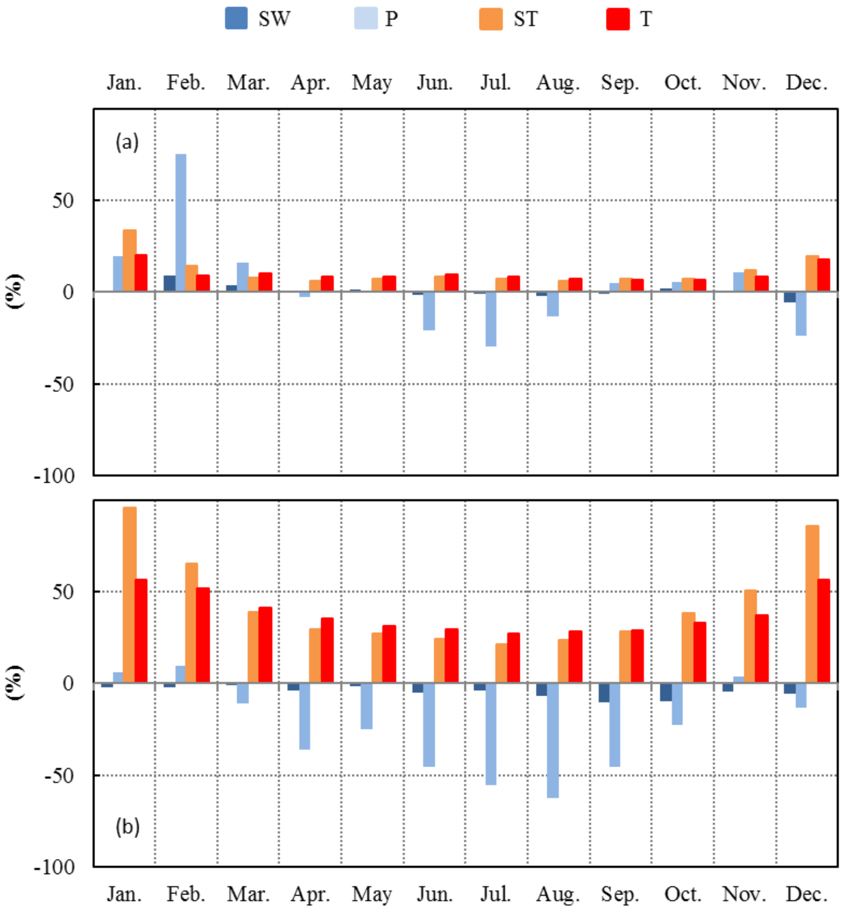
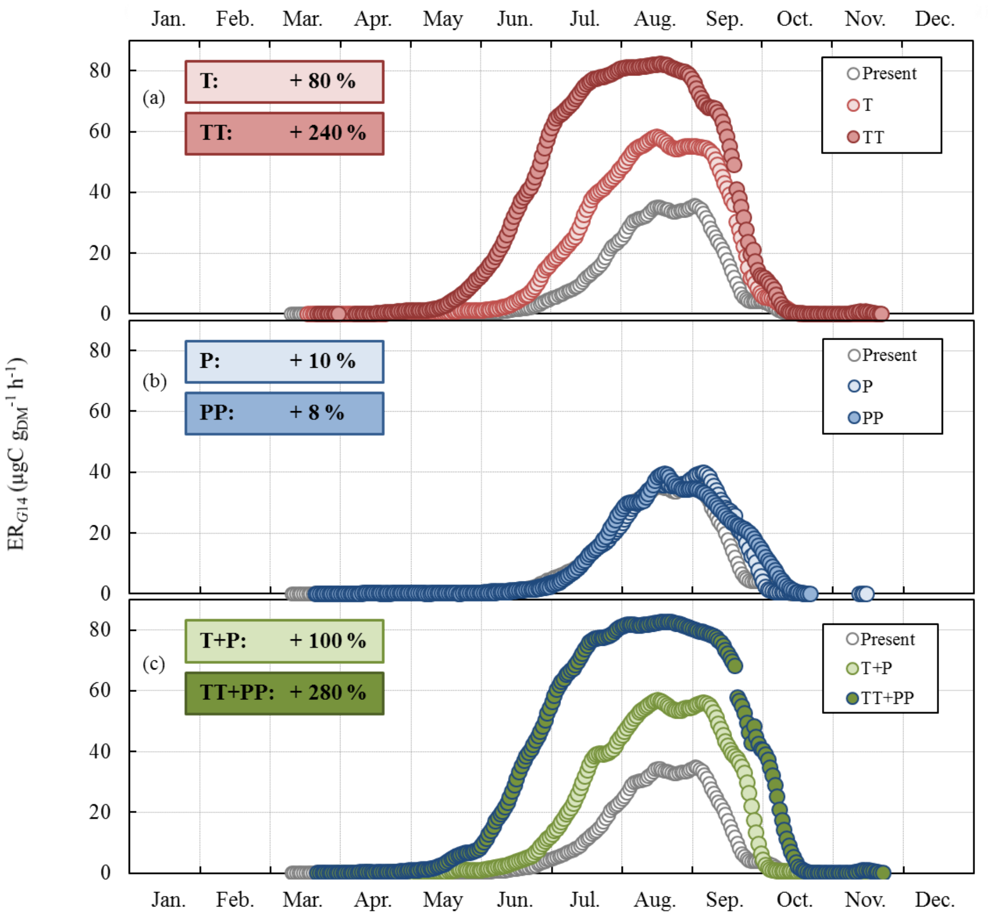

SW
P
ST
T
Jan.
Feb.
Mar.
Apr.
May
Jun.
Jul.
Aug.
Sep.
Oct.
Nov.
Dec.
(a)
(b)
(%)
50
0
-50
-100

Figure 8



Jan.
Feb.
Mar.
Apr.
May
Jun.
Jul.
Aug.
Sep.
Oct.
Nov.
Dec.
ER$_{G14}$ (µgC g$_{DM}$$^{-1}$ h^{-1})
(a)
T: + 80 %
TT: + 240 %
Present
T
TT
(b)
P: + 10 %
PP: + 8 %
Present
P
PP
(c)
T+P: + 100 %
TT+PP: + 280 %
Present
T+P
TT+PP
80
60
40
20
0

Figure 9

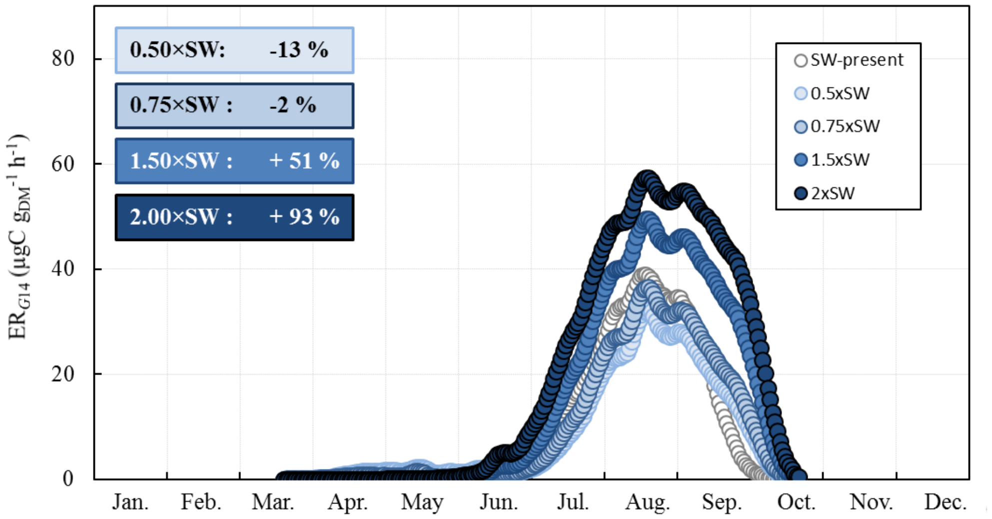

0.50×SW: -13 %
0.75×SW : -2 %
1.50×SW : + 51 %
2.00×SW : + 93 %
SW-present
0.5xSW
0.75xSW
1.5xSW
2xSW
ER_{G14} (µgC g_{DM}^{-1} h^{-1})
0
20
40
60
80
Jan.
Feb.
Mar.
Apr.
May
Jun.
Jul.
Aug.
Sep.
Oct.
Nov.
Dec.

Table 1

	ND		AD	
x	ER/ER_{MEGAN}=f(*x*)	R² value	ER/ER_{MEGAN}=f(*x*)	R² value
SW	$0.653e^{10.5x}$	0.13	$0.192e^{51.1x}$	0.66
SW-7	$0.715e^{1.30x}$	0.13	$0.239e^{6.30x}$	0.55
SW-14	$0.763e^{0.57x}$	0.11	$0.279e^{2.74x}$	0.48
SW-21	$0.523e^{0.46x}$	0.14	$0.365e^{1.47x}$	0.38

Table 2

	$\Delta\mathrm{SW}$	$\Delta Pcum$	$\Delta\mathrm{ST}$	ΔT	$\Delta\mathrm{SW}/\mathrm{SW}$	$\Delta Pcum/Pcum$	$\Delta\mathrm{ST}/\mathrm{ST}$	$\Delta T/T$
	(m^3 m^{-3})	(mm)	(° C)		(%)			
RCP2.6	+ 0.004	+ 30	+ 1.4	+ 1.4	+ 0.5	+5	+ 8.4	+ 9.1
RCP8.5	- 0.007	+ 30	+ 5.3	+ 5.3	- 5.0	-24	+ 32	+ 34

Formatted: Left, Space Before: 0 pt, After: 8 pt, Line spacing: Multiple 1.08 li